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THE FORMATION OF CRYSTALS IN GELS.*

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THE general properties of gels—or jellies—are familiar to us, but their inner structure is a matter of some dispute. J. M. van Bemmelin, Bütschli, and many others consider gels to be two-phase systems—a more concentrated solution as a network of cell-walls enclosing a more dilute solution of the same substance. The whole system is solid or semi-solid and extremely viscous. In the opinion of von Weimarn, the ultimate structure is minutely granular—even crystalline—and any coarser network is a secondary formation.

Emulsoids are two-phase liquids closely related to gels. In fact, emulsoids may change to solid gels by evaporation, cooling, or a change in the distribution of water, for example, between the two phases, thus altering their relative concentrations. Hot fluid emulsoids of agar or gelatine with water "set" to gels on cooling, but silicic acid gels set on the mere mixing of cold-water solutions of sodium silicate and a suitable acid. After standing some time the silicic acid forms two phases with the water, one more concentrated than the other, and when the proper distribution is reached solidification results. Manganese arsenate gels

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so rigid they hold their shape, unaided, as well as any fruit jelly also set without cooling or evaporation. The gels of ferric arsenate and ferric phosphate set on dialysis—a removal of acids, bases, and salts.

As a preface to a study of crystal formation in any of these gels we must note their retarding the rates of diffusion of acids, bases, and salts, and their prohibition of diffusion of colloids. The mesh structure of gels must be practically equivalent to a network of capillary channels filled with the less concentrated phase. It follows, then, that the presence of substances affecting the distribution of water between the two phases must affect the size of these channels and change the rates of diffusion above mentioned. For example, Hatschek states that such salts as citrates and sulphates produce more rigid gels, but iodides and sulphocyanates retard or prevent gel formation. Bechold adds that sulphates, glucose, alcohol, and glycerol retard diffusion, while urea, iodides, and chlorides accelerate it.

The influence of certain gels—or jellies—on crystal growth is illustrated by many crystalline minerals. It is very probable that gelatinous silicic acid was the ancestor of quartz and by gradual dehydration became hard silica rock. In the gelatinous medium reactions took place under conditions favoring the formation of crystalline veins. For example, the reduction of gold salts produced crystals of gold, veining the gel, which later became quartz. A convincing part of this development can be reproduced in the laboratory.

To the geologist a working method of duplicating many such processes of Nature must be of great value. To the chemist a study of reactions in gels gives a useful control of relative concentrations and velocity of reactions. The pathologist finds in the subject some relation to the formation of crystalline material in animal tissue.

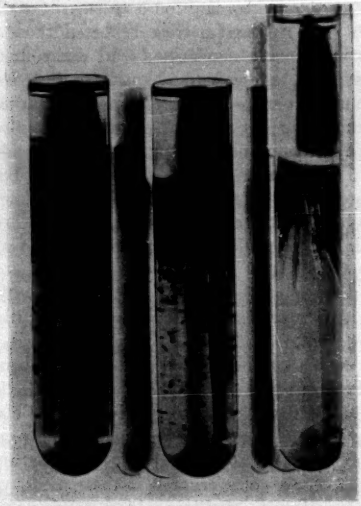
Silicic acid gels are discussed in this paper more than any other, but other gels function in a similar, though usually less effective, manner.

HISTORICAL.

E. Hatschek [1] did much important work in this field, attracted doubtless by the experiments of R. E. Liesegang. The latter ob-

[1] *Kolloid Z.*, 8, 193 (1911); *Ibid.*, 10, 77 (1912); *Ibid.*, 10, 124 (1912); *Ibid.*, 10, 265 (1912).

served that if a drop of silver nitrate solution was placed on a film of gelatine gel containing potassium dichromate the precipitated silver dichromate was formed in concentric rings separated by clear intervals. This "rhythmic banding" of "Liesegang's rings" will be discussed in a later paper. Whether a disk of gel or a tube partly filled with a gel be used, the essential feature is that one substance shall diffuse into a gel containing another



Mixed crystals of silver sulphate—silver chromate with silver dichromate below.

substance, with which it reacts to form a rather insoluble compound. Rhythmic bands may form or, under different conditions, separate crystals of remarkable size and shape.

Hatschek and Simon [2] reduced gold salts in silicic acid gels by the use of oxalic acid, ammonium formate, ferrous sulphate, sodium sulphite, carbon monoxide, sulphur dioxide, hydrogen, ethylene, etc. When illuminating gas was used as a reducing

[2] *Kolloid Z.*, 14, 115 (1914); *J. Soc. Chem. Ind.*, 31, 439.

agent a black deposit of carbon always appeared mixed with the gold. Since graphite sometimes occurs with gold in quartz veins, this experiment is suggestive.

Hatschek's usual method of work was to make a 5 to 20 per cent. gelatine gel or a 1 to 5 per cent. agar gel containing, for example, a small amount of potassium dichromate. This was allowed to solidify in a test-tube and covered with a solution of silver nitrate. The silver ion slowly diffusing down into the gel reacted with the dichromate ion to form silver dichromate in small crystals. In 1911 Hatschek reported these crystals 0.5 mm. long in 10 per cent. gelatine; lead dichromate 0.03 mm. long in 2 per cent. agar; lead chloride 2 mm. long in agar; barium carbonate 0.1 mm. long in 5 per cent. gelatine; potassium sulphate 0.2 mm. long in 5 per cent. gelatine. He also prepared a number of other crystalline compounds, such as lead iodide, lead sulphate, lead chromate, calcium sulphate, and barium silicofluoride. Later he used silicic acid gels as the media for diffusion, and obtained larger crystals. In 1913 he reported lead chloride crystals 15 mm. long. He was unable to make crystalline sulphides in gels.

His reduction of gold chloride in silicic acid with oxalic acid yielded beautiful crystalline gold and, by varying the conditions, colored colloidal gold.

Hatschek held that the concentration and nature of the gel determined the form and size of the crystals. The inelastic gels like silicic acid, he thought, were superior to the elastic organic gels like agar and gelatine. He wrote of "the practically universal tendency to form spherical bodies in agar and gelatine," although he did obtain some crystals in these media.

Hatschek [3] made gels of silicic acid by mixing sodium silicate solutions with hydrochloric acid. The diffusion of a lead salt into this gel formed crystals of lead chloride. In similar fashion he treated sodium silicate with sulphuric acid and caused lead or calcium salts to diffuse into the gel, thus forming crystalline sulphates of lead or calcium. With phosphoric acid gels he obtained crystalline phosphates of copper, calcium, and strontium.

Simon [4] grew the well-known "lead tree" in a silicic acid gel containing lead acetate. A bit of zinc or tin was pressed into the

[3] *Kolloid Z.*, 10, 77 (1912).
[4] *Ibid.*, 12, 171 (1913).

top of the gel. I found that if the gel is about 0.02 N with respect to lead acetate a splendidly branching tree grows and may be handled roughly, since it is supported on all sides by a solid.

Pringsheim [5] states that when two salt solutions diffuse into a gel in opposite directions the reaction does not proceed beyond a thin film if the solutions are isotonic. A hypertonic solution continues to diffuse into a hypotonic, and any precipitate formed is deposited in the latter. In accord with this idea, Hatschek often added indifferent substances to the solution on top of the gel in order to insure reaction below the gel surface.

Liesegang [6] found that the older opinion that growth of a precipitate in a gel was limited to one side of the initial precipitation film did not hold for quinol on silver nitrate. I confirmed Liesegang's finding by several new examples. He also obtained silver crystals in gelatine by reducing silver nitrate with ferrous sulphate.

Gerhart [7] placed a solid reacting substance in a test-tube, covered with a mixture of water-glass and a suitable acid before the gel set, and, after it became solid, poured a solution of the second reacting substance on top. Both salts then diffused into the gel and met. Gerhart found alum and potassium nitrate to have considerable influence on the form of crystals deposited.

Hausmann [8] obtained crystalline halides of thallium in gelatine.

Dreaper [9] dispensed with a gel as a medium for reactions and used a single capillary tube. For example, a capillary tube filled with 3 per cent. lead acetate was immersed in 5 per cent. hydrochloric acid. Crystals of lead chloride nearly 1 mm. long formed in the capillary. Sand in wide tubes functioned the same as a single capillary. Dreaper considered relative rates of diffusion and concentration of the incoming solution the determining factors.

Ernest Marriage [10] studied the arrangement and size of lead iodide crystals in fruit gels and jams. The various fruit jellies and jams influenced the precipitation of lead iodide in different

[5] *Z. phys. Chem.*, 17, 473 (1895).
[6] *Kolloid Z.*, 17, 141 (1915).
[7] *Tsch. Min. Mitt.*, 28, 347 (1908); *Ibid.*, 29, 185 (1910).
[8] *Z. anorg. Chem.*, 40, 110 (1904).
[9] *J. Soc. Chem. Ind.*, 32, 678 (1913); *Kolloid Z.*, 14, 163 (1914).
[10] *Kolloid Z.*, 11, 1 (1912); *Sci. Am. Sup.*, 77, 375 (1914).

ways, and use was made of this fact in detecting adulteration of commercial products.

De Schulten,[11] by the slow admixture of extremely dilute solutions of barium chloride and sulphuric acid, obtained crystals of barium sulphate that in a month measured 5 mm.

Deiss[12] prepared a gel of $MnHAsO_4$ by mixing equal volumes of 10 per cent. $MnCl_2$ and KH_2AsO_4. On standing three

Zinc-ammonio chloride crystals lining a dry cell.

months, rose-colored crystals of the same composition as the gel separated.

Kohler,[13] in a study of "rhythmic crystallization of sulphur," states that "the viscosity of the liquid must be so great that the rate of flow towards the crystallizing part is slower than the rate of crystallization." This compares with slowness of diffusion in a gel.

[11] *Compt. rend.*, 136, 1444 (1903).
[12] *Kolloid Z.*, 14, 139 (1914).
[13] *Ibid.*, 17, 10 (1915).

Shulansky and Gies [14] observed that " in the putrefaction of meat crystals of ammonio-magnesium phosphate appear early and accumulate rapidly," due to bacterial activity. This paper and a similar one by Perlzweig and Gies [15] may have some bearing on the subject because of the hydrated colloid nature of animal tissue.

Creighton [16] added the influence of a weak current of electricity to the process of diffusion in gelatine. Using an iron anode and a gel containing potassium ferricyanide, Turnbull's Blue appeared in stratified layers—not crystalline, however. Braun [17] believed that certain phenomena attending the formation of sulphides and the deposition of copper in capillary spaces previously noted by A. C. Becquerel are of an electrochemical nature, as Becquerel [18] had suggested: " Sur des noveaux effets chimique produits dans les action capillaire." These phenomena are partly dependent, according to W. Ostwald,[19] on the semipermeability of precipitated membranes.

In a paper on " Electrostenolysis," H. N. Holmes [20] reported on electrocapillary action in insoluble powders.

The observation of Henri Becquerel that solutions of copper sulphate and sodium sulphide meeting by diffusion through a fine crack in a glass tube formed minute crystals of copper sulphide relates to Dreaper's experiment with the single capillary.

Cornu's great series of papers [21] on the significance of gels in geology are an important part of the literature.

As will be shown elsewhere in this paper, slow diffusion processes in the earth's crust have much to do with the formation of crystalline mineral deposits. John Clark,[22] in " A Chemical Study of the Enrichment of Copper Sulphide Ores," gives a suggestive account of the reducing action of hydrogen sulphide and amorphous sulphur.

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[14] *Biochem. Bull.*, 3, 45 (1913).
[15] *Ibid.*, 3, 69 (1913).
[16] JOURNAL OF THE FRANKLIN INSTITUTE, 182, 745 (1916).
[17] *Ann. der Physik und Chemie*, 44, 507 (1891).
[18] *Compt. rend.*, 64, 919 (1867); *Ibid.*, 65, 51, 720 (1867); *Ibid.*, 66, 77, 245, 766, 1066 (1868); *Ibid.*, 67, 1081 (1868).
[19] *Z. phys. Chem.*, 6, 75 (1890).
[20] *J. Am. Chem. Soc.*, 36, 784 (1914).
[21] *Kolloid Z.*, vols. 1–5.
[22] *Bull. Univ. of N. Mex.*, 1, 79 (1914).

W. H. Emmons,[23] in a similar paper on "The Enrichment of Sulphide Ores," remarks, "To the chemist this paper is an appeal for more experimental data on the important mineral syntheses involved in the process."

P. Krusch[24] investigated primary and secondary ores with especial reference to the gel and the rich heavy metal ores.

Interesting changes in glass structure are given in U. S. G. S. Monograph 32, on "Spherulites and Lithophyse," and in a paper published by George H. Williams in an early issue of the *Johns Hopkins Circular*.

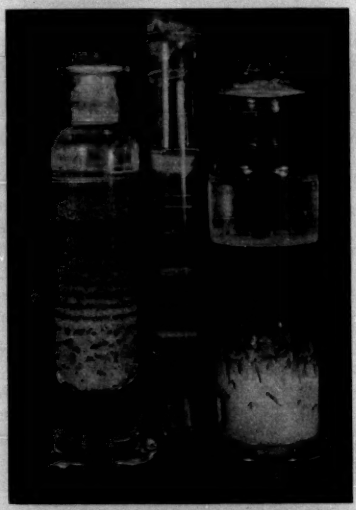
Johnston, Merwin, and Williamson,[25] discussing "The Several Forms of Calcium Carbonate," state that "aragonite is precipitated, as is well known, even at ordinary temperatures in a solution of a salt from which a carbonate isomorphous with aragonite may be precipitated. Aragonite is precipitated in the presence of a lead salt formed around nuclei of cerussite ($PbCO_3$) in parallel orientation." It seems to me that these authors might well try the precipitation of calcium carbonate in a neutral gel containing a lead salt. Crystals of unusual size might be obtained and thus facilitate their study.

Doelter[26] considers that practically all substances are colloidal when first precipitated. What we call amorphous bodies are very close to the crystalline. The tendency to pass from the colloidal to the crystalloidal condition is greatly influenced by pressure, shock, light, and long-continued heating. Doelter proved his point by laboratory experiments. He was led to declare that minerals whose formation was once thought to require high temperatures may easily be formed without such temperatures.

Stephen Taber,[27] in "The Origin of Veins of Asbestiform Minerals," makes a valuable contribution to the study of crystal growth. "The shape of a growing crystal is controlled by one or more of three independent factors, namely: (1) The tendency to assume a regular polyhedral form because of the forces of surface tension and molecular orientation; (2) the relative and absolute magnitude of the external forces resisting growth in

[23] *Bull. U. S. G. S.*, No. 529, 11.
[24] *Min and Sci. Press*, 107, 418 (1913).
[25] *Am. J. Sci.*, 41, 473 (1916).
[26] *Kolloid Z.*, 8, 29, 86 (1911).
[27] *Nat. Acad. Sci.*, 2, 659 (1916).

different directions; and (3) the accessibility of the material from which the crystal is built. As a result of the first factor some substances normally crystallize in slender, acicular or hair-like forms, but an asbestiform structure is never produced without the assistance of one of the other two factors. Crystal growth under unequal pressure undoubtedly explains the development of fibrous structure in some instances. The solubility of most substances increases with the pressure, and therefore crystal growth



Basic mercuric chloride in silicic acid containing an excess of base.

may be limited to the direction of least pressure. This hypothesis is not applicable, however, to fibres that develop normal to the walls of the vein. Moreover, the veins frequently intersect and run in all directions through a given rock mass. Such occurrences of abnormal fibrous structure must therefore be attributed largely to the circumstance that the material for growth was accessible only in one direction."

In another paper on "Pressure Phenomena Accompanying the

Growth of Crystals" Taber[28] remarks: "Crystallization is retarded or prevented in supersaturated solutions which occupy small capillary or subcapillary spaces; therefore crystals may be supplied with material for growth by diffusion through solutions occupying such spaces, and the increase in volume due to the entrance and deposition of new material must result either in the expulsion of part of the solution or the enlargement of the space occupied by the growing crystals. . . . Crystals grow in directions in which external forces oppose growth whenever the surfaces under pressure are in contact with a film of supersaturated solution, and it is possible to supply the material for growth by slow diffusion through subcapillary spaces, as great resistance is offered to the expulsion of solution from such openings. The conditions requisite for crystal growth under pressure commonly obtain in the rocks of the earth's crust, and many phenomena connected with the metamorphism of rocks, the growth of concretions, and the formation of mineral deposits are difficult of explanation under any other hypothesis than that growing crystals have made room for themselves by exerting pressure on the surrounding material."

METHODS OF WORK.

I found it convenient to mix equal volumes of solutions of sodium silicate and some acid, pouring the water-glass into the acid and mixing quickly and thoroughly. Before the silicic acid set to a solid one of the reacting salts was mixed with this solution, which was then poured into test-tubes. After the gel set, the other salt solution designed to react with the first was poured on top. The solution on top should have a greater osmotic pressure than the gel to insure reaction within the gel instead of above the surface.

The water-glass used was a commercial grade known as "water white," with a density of 1.375. The ratio of the Na_2O to the SiO_2 was 1 to 3.5. When diluted to a density of 1.06 and titrated against hydrochloric acid, using phenolphthalein as an indicator, it was equivalent to 0.51 N acid. With methyl red as indicator the normality was 0.57.

This particular water-glass was used at the 1.06 density for many experiments because weaker solutions were too slow in the

[28] *Ibid.*, 3, 297 (1917); *Am. J. Sci.*, 41, 532 (1916).

set of the silicic acid. With this concentration an equal volume of N acetic acid was suitable for most of the experiments. Such a gel set over night and contained a small excess of acid. It was reasonably clear. This rather arbitrary selection really marked the lowest concentration limit for working convenience. Acetic acid, 0.75 N, serves as well and gives less excess acid. Several other acids were used for special purposes, but the time of set varied with the acid. A partial list follows:

1.06 density sodium silicate with equal volume N acetic acid set in 6 hours.
1.06 density sodium silicate with equal volume N formic acid set in 36 hours.
1.06 density sodium silicate with equal volume NN phosphoric acid set in 10 minutes.
1.06 density sodium silicate with equal volume N hydrochloric acid set in 10 days.
1.06 density sodium silicate with equal volume N sulphuric acid set indefinite.
1.06 density sodium silicate with equal volume N nitric acid set in 4 weeks.

This applies only to the particular water-glass described above. Considering convenience in time of set, clearness of the gel, and failure to split as the gel contracts, the following table will be found more useful, except in respect to acetic:

1.16 density sodium silicate with equal volume 3 N acetic acid set in 1 hour.
1.08 density sodium silicate with equal volume of 3 N formic acid set in 48 hours.
1.06 density sodium silicate with equal volume 2 N hydrochloric acid set in 5 days.
1.06 density sodium silicate with equal volume 6 N sulphuric acid set in 1 day.
1.10 density sodium silicate with equal volume 2 N nitric acid set in 2 days.

Temperature changes affect the time of set considerably. I made a few tests with water-glasses of different composition and found it possible to get good results with them also. In one the ratio of Na_2O to SiO_2 was 1 to 2, its density 1.69, and, diluted to 1.06, the solution was equivalent to 0.67 N acid with phenolphthalein as indicator. In another the ratio of Na_2O to SiO_2 was 1 to 4, the density 1.34, and, diluted to 1.06, the solution was equivalent to 0.46 N acid.

New tables of time of set should be constructed on the basis of the normality of the particular water-glass at hand. For

example, a 1.06 water-glass equivalent to 0.67 N acid must be mixed with an equal volume of more than N acetic acid to give results similar to those in the table.

Pouring the mixture before it solidifies into the bend of a U tube gives the experimenter excellent control of conditions. The two reacting solutions poured separately into the arms of the U tube slowly diffuse through the gel and meet, often forming a

Silver dichromate crystals in alundum powder.

sharp precipitation band. Any amount of either solution can be used in this method.

Hatschek, in some of his work, directs that the mixture of water-glass and acid be dialyzed to free it from excess acid and salts. Addition of very little ammonia sets the gel. In other experiments he did not dialyze. I do not find it necessary or desirable to dialyze out the acid and salts. Their influence on crystal formation or development of banding is beneficial in most instances. In a number of experiments I used a large excess of

acid, and in others added salts or non-electrolytes to secure certain effects.

Doryland [29] suggested that a mixture of water-glass and just enough acid to make a neutral solution would set to a gel in minimum time. Traube and Kohler [30] came to a similar conclusion in regard to the effect of acids and bases on gelatine. This led me to make basic gels by using less acid than enough to neutralize the sodium silicate. In this way a very profitable field of investigation was opened up. Basic salts, for example, may not be studied in gels containing excess acid. A mixture of equal volumes 1.06 density water-glass and 0.5 N acetic acid is very slightly basic and sets in about three minutes. Other water-glasses must be titrated to get similar figures.

EXPERIMENTAL PART.

Hatschek's gold was so interesting and spectacular that it seemed advisable to vary his methods. He used a sodium silicate-hydrochloric acid gel with oxalic acid as a reducing agent. Phosphorus in ether, as well as a number of other reducing substances, was also tried by Hatschek.

After duplicating a number of his results I varied the acid used in making the silicic acid gel and secured by far the most spectacular effects when the gel was made by mixing sodium silicate with sulphuric acid. That this was due in part to the presence of sulphate was proved by comparing an oxalic acid reduction of gold chloride in a water-glass-acetic acid gel with a similar one containing, in addition, considerable sodium sulphate. The first gave very little crystalline gold—mostly the colored colloidal form. Addition of soluble sulphate developed a few color bands in the second.

To secure a dazzling display of gold crystals which gleam brilliantly in the sunlight, I found the best way was to mix equal volumes of 1.06 density sodium silicate and 3 N sulphuric acid. To 25 c.c. of this mixture 1 c.c. of 1 per cent. gold chloride was added. This gel set in about one week. Then the solid gel (in a test-tube) was covered with 8 per cent. oxalic acid solution. In several hours the crystal growth was marked, and in a few days at its best.

[29] Private communication.

[30] *Intern. Zeitsch. phys.-chem. Biol.*, **2**, 42 (1915).

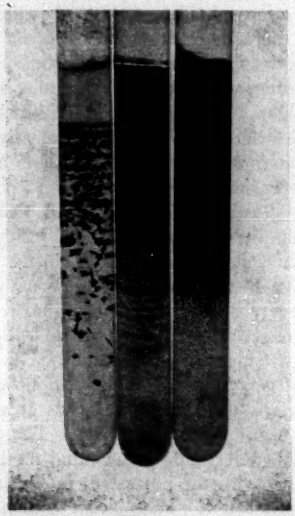
A remarkable difference appeared when 1.16 density water-glass was used instead of 1.06 with the 3 N sulphuric acid. With the same reducing solution—8 per cent. oxalic acid—a series of splendidly colored bands of colloidal gold was obtained. The upper layer of the first bands was red, below that blue, and below that green. A comparatively clear gap below this was followed by another red-blue-green zone. Usually after the first few rainbows the red was omitted. A dozen or more such bands in an ordinary test-tube were not uncommon—the upper bands measuring about 1 cm. in depth. Golden crystals were dispersed all through these gels, but it should be noted that the 1.06 water-glass-3 N sulphuric rarely developed colored colloidal gold—only the yellow crystals.

Many variations in concentrations were tried. Excellent results were obtained with 0.5 c.c. of 1 per cent. gold chloride in 25 c.c. of gel, but 2 c.c. was not so good, and with much less than 0.5 c.c. the gold was too thin. Even 2 per cent. oxalic acid was effective as a reducer, but a saturated solution—about 8 per cent.—was most satisfactory. A very little gum tragacanth mixed with the gel to reduce the gold chloride resulted in blue colloidal gold uniformly distributed.

Copper.—Perfect tetrahedrons of metallic copper were obtained in a 1.06 water-glass-N acetic acid made 0.05 N with respect to copper sulphate. The gel was covered with a 1 per cent. solution of hydroxylamine hydrochloride. In a week or two the tetrahedrons were large enough to observe with the unaided eye. Those formed near the surface were much smaller than those at greater depths. Of course, the farther the reducing solution diffused into the gel the more dilute it became. In a beam of sunlight the faces of the tetrahedrons gleamed with a splendid copper lustre. In nearly all experiments one or more groups of overlapping tetrahedrons were noted. These formed in three radiating lines, making angles of 120 degrees, or in some instances of 60, 120, and 180 degrees. This arrangement of copper crystals is found in mineral deposits. All the other reducing solutions tried were inferior to hydroxylamine.

The presence of small amounts of glucose, cane-sugar, alcohol, or glycerol in the gel caused the formation of a good deal of red feathery stuff. The presence of sodium sulphate aided crystallization.

With a basic gel very different results were obtained. Glucose—a few grammes of 25 c.c.—was mixed with a 1.08 water-glass-0.5 N acetic acid gel and covered with 0.5 N copper sulphate. After a few months close bands of rather amorphous cuprous oxide extended down the gel for a distance of about 12 cm. At first the bands were yellow, but as they aged they turned to a dull red. At one time both colors were in evidence, the newer



The influence of chlorides on the distribution of mercuric iodide. The tube at the left contains sodium chloride—the others do not.

bands yellow. Near the surface of the gel a blue deposit of cupric hydroxide formed. This reaction is suggestive of Fehling's test for glucose. Of course, no copper complex is used here, but evidently slow diffusion permits the reduction from cupric hydroxide to cuprous oxide.

It has been suggested that this method gives opportunity for studying a reaction in its various stages. The control of concentrations and the rates of diffusion pave the way.

Using a U tube containing a 1.10 water-glass-0.5 N acetic acid gel in the bend and 0.5 N copper sulphate in one arm and 1 per cent. hydroxylamine in the other, blue-white bands with a yellow front appeared, later red cuprous oxide, and, finally, red tetrahedrons of metallic copper.

Silver Dichromate.—A 1.06 water-glass-N acetic acid gel was set in the bend of a U tube and the arms filled with 0.1 molar silver nitrate and 0.1 molar potassium dichromate. Minute dark-red crystals soon formed. In one test-tube experiment a single crystal of silver dichromate measured $5 \times 5 \times 1$ mm. This was after a few months' growth. In a U tube experiment a thin red sheet, 1 cm. long, was found—so thin that it was a clear red by transmitted light. Thicker crystals were almost black. The presence of very little gum tragacanth or starch in one of these gels hindered the formation of good crystals and favored the development of spherulites.

Lead Iodide.—Lead iodide crystals had been made by other investigators, but merited further study. This is one of the easiest to make and most spectacular of all the crystal exhibits. A 1.06 water-glass-N acetic acid mixture containing 2 c.c. of N lead acetate to every 25 c.c. was poured into test-tubes. After the silicic acid gel set firmly it was covered with 2 N potassium iodide. A compact layer of lead iodide quickly formed on the surface, followed very soon by crystallization below the surface of the gel. In a few days fern-like fronds grew down into the gel, mixed with many hexagonal plates. These concentrations may be varied with interesting results, and the lead salt may be used above the gel with the potassium iodide in the gel. The first order is much better. Magnificent golden fern fronds, 8 cm. in length, and nearly perfect hexagons, 5 mm. in diameter, were obtained in some experiments. In one or two tubes six hexagons grouped around a centre much like the arrangement in some snow crystals. On standing in direct sunlight for several months the lead iodide crystals blacken somewhat.

Using an excess of the lead acetate as compared with the potassium iodide, for example, in U tubes pouring 0.25 N lead acetate in one arm and 0.1 N potassium iodide in the other, with a gel separating the solutions, yellow-white needles and blocks of basic lead iodide formed. Some of the needles were 2 cm. in

length. Watts[31] states that if lead acetate in excess is mixed with potassium iodide the basic iodide forms unless sufficient acid is present to prevent. With lead nitrate the ordinary lead iodide results. When formed very slowly, the yellow-white needles and blocks gleam brilliantly and seem to have a high index of refraction. Star-shaped groups and crossed stick arrangements were common. This is not the white double salt ($PbI_2.KI.2H_2O$) made by Remsen and Herty[32] by the action of excess potassium iodide on lead iodide.

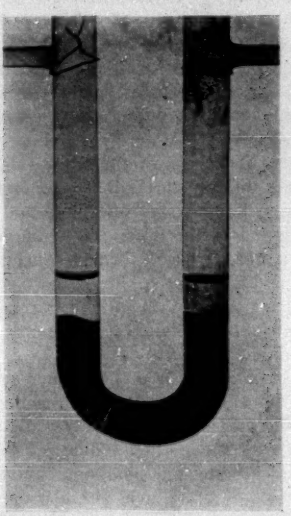
In U tube experiments such concentrations as 0.25 N lead acetate and 0.1 N potassium iodide formed both the ordinary yellow hexagons and, in the arm nearer the lead acetate, the white-yellow basic crystals. In fact, these concentrations could be so varied as to give, first, only the yellow crystals of lead iodide, with a later formation of the white-yellow basic iodide. As the lead acetate diffused through the gel and met the potassium iodide these yellow hexagons formed, and later, as excess lead acetate diffused into this zone, the white needles or blocks developed. Often a basic crystal formed, touching the edge of a yellow hexagon, and apparently "ate it up" as the excess lead acetate reached that point. With such proportions in the U tube as 0.25 lead acetate and N potassium iodide only the yellow hexagons of the normal iodide form.

In a slightly basic gel, such as 1.06 water-glass-0.5 N acetic, the formation of the white needles of the basic iodide was greatly favored. Dropping acid on these basic crystals instantly turned them yellow, forming the normal iodide. Using 0.25 N solutions of both lead acetate and potassium iodide in a U tube, a 1.06 water-glass-0.5 N acetic acid gel developed white needles in two days, growing to a length of 2 cm. in one week; a 1.06 water-glass-N acetic acid gel developed yellow hexagons in two days, and in one week white stars also appeared; a 1.06 water-glass-2 N acetic acid gel developed yellow hexagons in two days, and in several weeks no white crystal of the basic salt appeared. The last gel was too acid for a basic salt, while the first gel had a slight alkaline reaction.

A little starch paste mixed with a 1.06 water-glass-N acetic acid gel produced a most interesting result. The gel turned blue

[31] Dictionary of Chemistry, iii, 127.
[32] *Am. Chem. J.*, 14, 107 (1892).

around the individual crystals, proving the release of free iodine. It cannot be urged that the excess acid formed hydrogen iodide which was oxidized by dissolving oxygen, for in that event the gel would have turned a solid blue. It is possible that the starch intimately mixed with the lead iodide as it formed reduced part of it to lead subiodide. There is no question about the existence of a subiodide of lead as recently proved by Denham.[33]



Rhythmic bands of mercuric iodide in a silicic acid gel.

A very little gum tragacanth in the silicic acid gel caused the appearance of spherulites of lead iodide and greatly hindered crystallization. In scores of experiments lead iodide showed no tendency to band in silicic acid gels, although in agar well-marked bands of crystalline aggregates were the rule. Hatschek reports bands of lead iodide in silicic acid gels when he used tap-water in preparing solutions, attributing the effect to the bicarbonates present in the water.

[33] *J. Chem. Soc.*, 29 (1917).

Lead bromide in white twin crystals was prepared by experiments similar to those with lead iodide.

Mercuric Iodide.—A 1.06 water-glass-N acetic acid gel with a 0.1 N content of potassium iodide was covered with a saturated solution of mercuric chloride—approximately 0.5 N. At once a layer of red mercuric iodide formed on the surface of the gel, and later scarlet needles in a more or less banded arrangement, depending on relative concentrations. Some of these needles grew to one centimetre in length. Separate cubes of mercuric iodide were observed in some tubes. With a suitable concentration of potassium iodide in the gel, the growing mass of red crystals developed a yellow front, bounded by a sharply marked surface. This zone of yellow needle crystals advanced down the tube. In reality a new yellow zone formed and the old turned red.

An excess of mercuric chloride reacted with the red mercuric iodide to form a somewhat soluble double salt. As a result, the first zone of red crystals formed in the upper part of the gel finally disappeared as the excess of mercuric chloride from the solution above reached this zone. Reversing the order, mixing the mercuric chloride in the gel and allowing the potassium iodide to diffuse down into the gel, produced a mass of red crystals as before, but the red zone advanced down the tube at a rapid rate. In reality a new front formed and the excess potassium iodide readily dissolved the rear of the mercuric iodide column.

With suitable concentrations wonderful banding of red mercuric iodide was obtained. Some tubes contained 40 bands in a distance of 8 cm. The spaces between the denser bands contain scattered crystals. The U tube method was very useful here. Red bands advanced around the bend as the excess of mercuric chloride diffused into the gel. When sufficient mercuric chloride was supplied the red bands finally disappeared, leaving alternate opaque white and clear spaces in a replica of the original banding. Mercuric nitrate diffusing into similar gels produced much better banding than did mercuric chloride, possibly due to the difference in ionization. The presence of sodium nitrate aided banding considerably, as did sugar.

Sodium chloride showed a striking influence on the arrangement and form of the crystals of mercuric iodide. In proportion to the amount of sodium chloride added to the silicic acid

gel the crystals of mercuric iodide became much larger and more like cubes than needles. They were farther apart, and less of the banding arrangement was noticeable. In another series of experiments the acetic acid was dispensed with in making the gel. Water-glass of 1.06 density and 2 N hydrochloric acid made 0.1 N with respect to potassium iodide was poured into tubes, and, after the silicic acid became solid, was covered with saturated mercuric chloride. The red crystals of mercuric iodide formed were very large, relatively, far apart, and no bands could be seen. This change was due to the influence of chlorides, for sodium chloride was formed in the reaction making the gel and, in addition, an unusual excess of hydrochloric acid was present. With less of the same acid the change was not so marked.

A little starch paste in the silicic acid gel caused the appearance of blue around the individual crystals, proving—as with lead iodide—the presence of free iodine at the surface of the crystals. This, too, may be a reduction of the mercuric iodide by the starch.

Basic Mercuric Chloride.—In attempting to make mercuric iodide in a slightly basic gel, 1.08 water-glass-0.5 N acetic, magnificent brown-black leaves were observed, some of them 2 cm. in length. These leaves appeared in the arm of the U tube containing the mercuric chloride. They formed very soon before any potassium iodide could diffuse into that part of the gel. Other mercuric salts gave no such result, so to test the matter I poured a basic gel, 1.08 water-glass-0.5 N acetic into a test-tube and with no other added salt covered the gel with saturated mercuric chloride solution. The same shining red-brown leaves appeared. Since they could not be obtained in a gel of acid reaction nor with any salt other than mercuric chloride, they were evidently one of the basic mercuric chlorides. A search of the literature justified this theory. Different basic chlorides are on record, but the description of $HgCl_2.2HgO$ agrees perfectly with the crystals obtained above.

Gels of different basicity were covered with mercuric chloride solution and the crystals compared. With 1.06 water-glass-0.5 N acetic (very slightly basic) the crystals were more widely scattered and, at a distance of a few centimetres from the surface of the gel, were excellent. This particular gel caused the most remarkable banding of the basic chloride. With a very

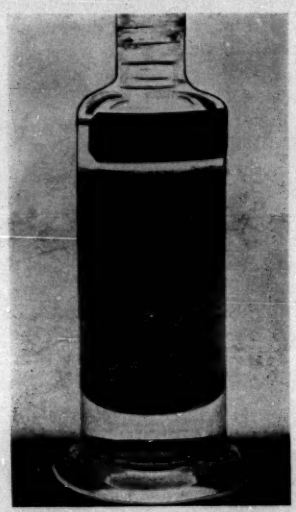
basic gel the crystals were smaller and formed in a rather compact mass. A few grammes of glucose in 25 c.c. of a slightly basic gel changed the results decidedly. Instead of the brown-red leaves, a gray mass of closely-packed bands, sharply marked, appeared. In a distance of 8 cm. over one hundred of these bands were counted.

Silver Sulphate.—An attempt was made to produce silver dichromate by allowing N silver nitrate to diffuse into a silicic acid gel containing very dilute potassium dichromate. This particular gel was the result of mixing 1.06 water-glass with 3 N sulphuric acid instead of the usual acetic acid. Immediate formation of bright-red crystals at the top of the gel was observed, and later the usual black-red silver dichromate deeper in the gel. Curiously enough, the bright-red crystals were of an entirely different system, orthorhombic, from the triclinic silver dichromate below. They grew rapidly—in less than one hour their shape was apparent, and over night they grew to a length of one centimetre. In a week or two, by using more concentrated silver nitrate, slabs 3 cm. long were obtained, but in spite of their thickness they were a clear cherry red. Using 0.1 N silver nitrate no such orthorhombic crystals formed, only the ordinary silver dichromate. The gel had to be made with sulphuric acid and water-glass. This suggested a double salt formed with the excess of silver nitrate, but the difficulty was readily cleared by analysis and further experiment. Analysis showed the red orthorhombic crystals to be almost entirely silver sulphate, with a very little silver chromate mixed in.

Chamot [34] states that both silver sulphate and silver chromate are orthorhombic, hence these must be mixed crystals. Gooch [35] and Autenrieth [36] observe that silver chromate is formed when excess silver nitrate reacts with a soluble dichromate, hot or cold. To test the mixed crystal explanation, I omitted the potassium dichromate in another experiment and secured colorless slabs exactly like the cherry-red ones in shape and time of formation. Furthermore, by the presence of a single drop of a potassium dichromate solution in a tube of the gel a faint yellow color was made to appear in the slabs. Their depth of color was easily

[34] "Elementary Chemical Microscopy," 335.
[35] "Methods in Chemical Analysis," 406.
[36] *Ber.*, 35, 2057.

made to vary with the concentration of the potassium dichromate. No doubt this experiment could be extended to many other pairs of isomorphous substances. The conclusion is that when approximately N solution of silver nitrate diffuses into a silicic acid gel made from 1.06 water-glass and 3 N sulphuric acid containing any small amount of a soluble dichromate mixed crystals—not a double salt—of silver sulphate and silver chro-



Basic lead iodide in a silicic acid gel.

mate result. As the silver nitrate becomes more dilute at greater depths in the gel only the normal silver dichromate forms.

Silver Acetate.—The silver sulphate experiment is very similar to one with silver acetate. Increasing the concentration of silver nitrate to N in making a silver dichromate, I found that gels made from acid and water-glass soon showed long, colorless slabs or leaves. Omitting the potassium dichromate from the experiment, and simply allowing N silver nitrate to diffuse into a 1.06 water-glass-N acetic acid gel, the same colorless leaves were produced again. Analysis showed them to be silver

acetate. In ten minutes these crystals grew a few millimetres in length, and over night to one centimetre.

By varying the acid mixed with the water-glass in making the silicic acid gel and allowing approximately N silver nitrate to diffuse in, many silver salts can be obtained in crystalline form. This principle was applied by Hatschek to other compounds.

Silver phosphate formed in this manner (1.06 water-glass to 3 N phosphoric acid) grew in irregular yellow fronds, very much like minute ostrich plumes.

Acid potassium tartrate crystals grew rapidly when a 1.16 water-glass-3 N tartaric acid gel was covered with any dilute potassium salt solution. Blocks 5 mm. wide resulted, and in several hours crystals of notable size could be counted on. Changing the concentrations somewhat, wide-branching fern growths were obtained.

Dihydrogen monosodium phosphate crystals formed when about 3 grs. of disodium phosphate were mixed with 10 c.c. of a 1.10 water-glass-2 N acetic acid gel. In a cool room perfect colorless rhombohedrons appeared in a few hours and grew to 6 mm. width in two days. These crystals were so soluble that as the room warmed they dissolved. On cooling in the ice-box they appeared again, but not in such good crystals. Some of the attempts to duplicate this experiment failed. Exact temperature and concentration conditions were not studied.

Urea nitrate crystals of large size formed rapidly when concentrated nitric acid mixed with an equal volume of water diffused into a 1.06 water-glass-N acetic acid gel containing urea.

Lead chromate and basic lead chromate developed in a slightly basic gel such as 1.06 water-glass-0.5 N acetic acid containing a little potassium chromate when lead acetate solution diffused into the gel. In a few weeks a 15-cm. test-tube filled with orange tendrils curling around countless brighter yellow crystals of minute size. In addition, much of the orange material concentrated in regular bands about 5 mm. apart. Near the top of the gel an orange-red band one centimetre deep developed. This, of course, was basic lead chromate. Hatschek formed lead chromate in a gel of acid reaction and thus missed the opportunity of making the basic chromate.

Barium carbonate formed in a basic gel containing some

sodium carbonate. A silicic acid gel was covered with a solution of a barium salt. The crystalline character of the deposit was not apparent for some time. White spherulites appeared to a depth of about 5 cm., and then flower-shaped crystalline aggregates formed. They were very small, but the crystalline character was apparent to the unaided eye.

Potassium bisulphate crystals of considerable size appeared in a gel formed by the "Hopkins process"[37] of obtaining soluble potassium salts and aluminum sulphate from feldspar. Finely ground feldspar was heated at 300° with moist potassium hydroxide. This partial decomposition of the feldspar was then completed by reaction with sulphuric acid. In commercial practice hydrochloric acid is used at this point. Using sulphuric acid in a mere laboratory experiment, a silicic acid gel formed and crystals of $KHSO_4$ grew in this medium.

Sugar crystals often appear in ordinary fruit jellies. I have a number that measure about $5 \times 7 \times 9$ mm.

Calcium tartrate crystals of great beauty, $20 \times 5 \times 5$ mm., were easily obtained in a U tube containing a 1.06 water-glass-0.5 N acetic acid gel by filling one arm with a solution of calcium chloride and the other with a solution of tartaric acid.

Copper tartrate crystals of perfect shape and clear blue color were made by covering a 1.06 water-glass-3 N tartaric acid gel with 0.5 N copper sulphate.

Zinc-ammonio chloride crystals of several centimetres in length were found in the gelatinous packing next the zinc wall of commercial dry cells. These colorless sheets are of the formula $ZnCl_2.2NH_3$. They were also obtained by Marignac in a Leclanche cell, but not of such large size. The starch paste or other gelatinous filling next the wall of a dry cell regulates the diffusion rates of the zinc chloride and ammonia formed by the chemical action of the battery on discharge, thus greatly aiding crystal development. On short periods of service, with rest intervals, these crystals were longer than in batteries run down by continuous service. This agrees with the time feature of the theory proposed in this paper.

DEVELOPMENT OF A THEORY.

Early in my work I decided that the most important feature of the favorable influence of gels on reactions forming crystals

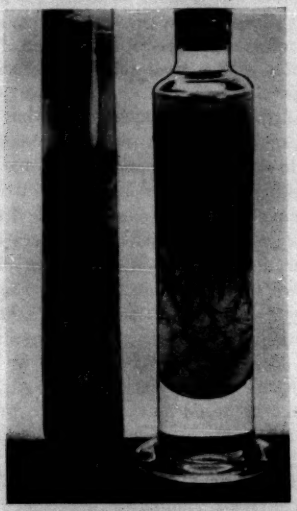
[37] Holland, Frazer, Miller, U. S. Patent 1,196,734.

was the capillarity of the gel structure. To test this, I used a layer of finely powdered silica in a U tube, soaked it with water to dislodge air, and filled one arm with a solution of potassium dichromate and the other with a solution of silver nitrate. Slow diffusion of the two salts through the capillary spaces between the silica grains allowed the formation of good crystals of silver dichromate. Later I learned that Dreaper had already developed that idea, using not only a layer of sand, but a single capillary tube. It may be objected that the rather great surface of finely divided silica permits an appreciable solution of silica, thus filling the space pores with a weak gel of silicic acid. Coarse sand did not serve so well.

It seemed worth while to extend somewhat the list of substitutes for gels in this work, so flowers of sulphur was substituted for sand in the above experiment. Some trouble was experienced in packing the sulphur in the bend of the U tube, and many attempts failed from too close packing for free diffusion. A platinum wire was used to dislodge the persistent air bubbles. Finally an excellent band of red crystals of silver dichromate formed where the silver ion met the dichromate ion. Barium sulphate and alundum powder served much better than the sulphur as substitutes for a gel. In fact, the results with alundum were startling. Silver dichromate formed in flat needles one centimetre in length. Closely-packed asbestos gave fair results. Certainly it cannot be urged that any gel was present in the experiments with a membrane of sulphur or alundum or barium sulphate.

Without doubt, any compact mass of insoluble discrete particles with proper sized capillaries will function as a gel in favoring the formation of crystals. Other influences may be present in a true gel. Adsorption, pressure, and solubility effects may greatly influence the capillary space results. A rather amorphous insoluble compound first formed by the meeting of two reacting substances in a relatively narrow channel may so further regulate the rates of diffusion as to give time for crystal formation of more of the same insoluble compound. In this suggestion the geologist may possibly find an explanation of the marked crystalline nature of some mineral veins. The pathologist, too, may obtain some light on the accumulation of crystalline deposits in animal tissue.

To test the theory, the mouth of a small specimen tube was covered with a sheet of goldbeater's skin, holding it on firmly with a rubber band. The tube had first been filled with a solution of 0.1 N potassium iodide. Care was taken to leave no air bubbles on the under side of the membrane and to rinse the outside of the tube. The tube was then immersed in a small beaker of saturated lead acetate solution. At once an almost amorphous



"Lead trees" in silicic acid gels.

precipitate of lead iodide appeared on the under side of the membrane, and in less than a minute crystals of lead iodide fell in a beautiful gleaming shower, rapidly increasing in amount. It is very easy to secure gleaming crystals of lead iodide by cooling its hot solution, but in this experiment the solutions were cold. Mixing the same solutions in a test-tube without the use of a membrane, a yellow powder results.

If the more concentrated solution was placed inside the specimen tube, the crystals formed on the upper surface of the mem-

brane. This is in accord with the osmotic difference rule of Pringsheim. With less difference in concentration of the reacting substances solutions the reaction was much slower.

Separating solutions of silver nitrate and potassium dichromate in this way, it was a simple matter to make a gramme or two of brilliant crystals of silver dichromate settling to the bottom of the tube. Possibly this method may be of some use in the preparation of pure compounds, since the crystals are not mixed with an annoying gel. Other thin, semipermeable membranes serve. Parchment paper is good, but goldbeater's skin is most suitable.

In a number of experiments it was observed that at first a rather amorphous or, at least, fine-grained precipitate formed on the surface of the original membrane, thus forming a new membrane of different capillary structure which exerted a marked influence on rates of diffusion. The result of checking the rates of diffusion of the reacting substances was to give time enough for the growth of minute particles to crystalline size.

Barium sulphate is most annoying in quantitative analysis because of its tendency to form in slow settling colloidal suspensions. It seemed an interesting experiment to precipitate it by the diffusion cup method and observe the rate of settling. I believed that if I placed a dilute solution of a sulphate inside the specimen tube, covered it with a goldbeater's skin touching the surface of the solution, and immersed the tube in a more concentrated solution of a barium salt, the barium sulphate formed on the under side of the membrane would be of much larger crystals than usual and would settle rapidly. It did. Some modification of this experiment may possibly be applied to the determination of sulphates.

To carry the theory further, the only need of the goldbeater's skin is to prevent sudden wholesale mixing of the solutions and mechanically sustain the rather amorphous precipitate first formed, which then functions as the real active membrane. This theory is not universal in its application, for in gels excellent crystals of a number of substances formed without the appearance of a preliminary compact layer of precipitate. In these instances only the gel functions in regulating diffusion. The theory does apply, however, in the absence of a gel and in all instances where a compact precipitation band is formed.

John Johnston's method of preparing crystals of increased size by the slow diffusion of two reacting solutions in a large volume of water at two widely separated points supports the theory above given. De Schulten's experiment, described earlier in this paper, is somewhat similar to Johnston's.

The usual gels employed in earlier investigations were agar, gelatine, and silicic acid. To this list I added the insoluble powders above described, and also gels of ferric phosphate and manganese arsenate. Both of these permitted the formation of good crystals of lead iodide, silver dichromate, and mercuric iodide. It is noteworthy that they are inorganic gels like silicic acid. Probably the protective colloid action of organic gels hinders crystal growth.

It is not necessary that this subject be limited to gels. Since the influence of gels on crystal formation is largely that of regulated diffusion, it is permissible to discuss even such structures as steel. Alexander [38] holds that graphite in steel is partly in the colloidal form and therefore inhibits crystallization. It would seem that films of colloidal graphite around crystalline nuclei of cementite, for example, must greatly influence the growth of those crystals when steel is cooled from a high temperature. Colloids in general retard diffusion. But, instead of inhibiting crystallization, as Alexander believes, it is conceivable that, although cementite crystals in the steel may form more slowly, they may be larger and of different shape than if formed rapidly.

Ice-cream without egg-white or gelatine or some other protective colloid is grainy. Of course, the lactalbumin in the milk is a protective colloid, but there is not enough of it. In marshmallows crystallization of the sugar is prevented by the protective colloid effect of gelatine or gum arabic.

The reduction of gold or copper salts in plastic glass with the production of a ruby tint is somewhat related to this topic. Possibly new ornamental effects could be obtained by experimenting with diffusion zones while the glass is hot enough to be plastic. Of course, the glass in that condition is not a gel, but it permits slow diffusion.

There seems no good reason why many very viscous substances should not function as gels in their influence on diffusion reactions.

[38] *J. Soc. Chem., Ind.*, **28**, 280.

SUMMARY.

1. Good crystals of silver dichromate were obtained by allowing the slow diffusion of solutions of silver nitrate and potassium dichromate through flowers of sulphur. Barium sulphate powder served as well, and alundum was even better. This confirms Dreaper's opinion that diffusion through capillary spaces other than those in a gel may be efficient in aiding crystal formation.

2. An experiment was devised to prove that in many instances the amorphous or fine-grained precipitate formed when two solutions meet acts as a membrane or network of capillaries, retarding further diffusion and favoring the formation of more of the precipitate in larger crystalline particles.

3. Silicic acid gels of alkaline reaction were made by mixing sodium silicate with less than enough acid for neutralization. These basic gels made possible the production of crystalline salts not possible in a gel of acid reaction.

4. Gold in a beautifully crystalline condition was best prepared by mixing equal volumes of a water-glass, 1.06 density, and 3 N sulphuric acid, adding 1 c.c. of 1 per cent. chloride to 25 c.c. of the mixture and, after solidification of the gel, covering with a solution of 8 per cent. oxalic acid.

Startling rainbow bands of red, blue, and green colloidal gold, mixed with scattered crystals, resulted when the water-glass was 1.16 density. Both methods worked readily and gave better results than any yet recorded.

5. Perfect tetrahedrons of copper were secured by using 1 per cent. hydroxylamine hydrochloride to reduce dilute copper sulphate in a silicic acid gel. Peculiar aggregates of tetrahedrons similar to those found in copper deposits in Nature were also observed.

All the steps of the reduction of cupric hydroxide to yellow and red forms of cuprous oxide were shown simultaneously in a series of many bands, using glucose as the reducing agent in a silicic acid gel of alkaline reaction. With 1 per cent. hydroxylamine the same reduction was carried through the cupric hydroxide and cuprous oxide to tetrahedrons of metallic copper. This suggests a method of controlling the different steps of other reactions for study.

6. Lead iodide in perfect hexagonal plates, 5 mm. wide, and

golden, fern-like growths, 8 cm. long, were formed in silicic acid gels. A basic lead iodide in yellow-white needles, 2 cm. long, formed by the action of excess lead acetate on potassium iodide in a slightly acid gel and even better in a slightly basic gel. Iodine was released on the surface of crystals of lead iodide, as shown by the presence of a little starch mixed with the silicic acid. Some reduction of lead iodide must have taken place, possibly caused by the starch.

7. Red mercuric iodide in 2 cm. needles or, in smaller crystals, banding in as many as forty regular bands in a distance of 8 cm. was obtained by the diffusion of a mercuric chloride solution into a silicic acid gel containing potassium iodide. With certain concentration conditions yellow crystals formed in front of the red needles and were finally changed into the red mercuric iodide. Soluble chlorides exerted a striking influence on the size, form, and arrangement of the mercuric chloride crystals.

8. Magnificent red-black crystals of a basic mercuric chloride resulted when a saturated solution of mercuric chloride diffused into a silicic acid gel of slightly basic reaction. In a very slightly basic gel these crystals were grouped in a remarkable series of bands. The presence of a little glucose exerted a marked influence, changing the color and developing over one hundred compact bands in a distance of 8 cm.

9. Silver sulphate crystals appeared in less than one hour when N silver nitrate diffused into a silicic acid gel made by mixing equal volumes of 1.06 density water-glass and 3 N sulphuric acid. In a few days orthorhombic slabs, 3 cm. long, developed If enough potassium dichromate to make the whole gel 0.1 N molar with respect to this salt only was present, the long slabs were a beautiful clear red. In the presence of excess silver nitrate near the surface of the gel silver chromate was formed, and, since silver chromate and silver sulphate are isomorphous, red mixed crystals resulted. The color of the crystals was made any depth of red by varying the concentration of the potassium dichromate in the gel. Farther below the surface of the gel the silver nitrate became less concentrated, and triclinic crystals of the red-black silver dichromate appeared. In time they grew to a size $5 \times 5 \times 1$ mm.

10. Silver acetate grew in gleaming white sheets, 2 cm. long, when N silver nitrate diffused into a silicic acid gel made from

water-glass and acetic acid. These crystals appeared in a few minutes. Such protective colloids as gum tragacanth, when present in very small amounts, twisted the straight crystals of silver acetate into fantastic shapes.

11. Basic lead chromate was made in crystalline bands by diffusion of lead acetate solution into a silicic acid gel of alkaline reaction containing potassium chromate; urea nitrate in large crystals, by the diffusion of nitric acid into a silicic acid gel containing urea; perfect crystals, 5 mm. wide, of acid potassium tartrate and perfect crystals of copper tartrate in a silicic acid gel made with tartaric acid; and monosodium phosphate in large, colorless rhombohedrons by mixing disodium phosphate in a sodium silicate-acetic acid gel.

12. Dry batteries discharging for short intervals developed colorless slabs, several centimetres in length, of $ZnCl_2.2NH_3$ next the zinc wall of the container. The gelatinous paste in this part of the cell caused slow diffusion of the zinc chloride, and ammonia formed by the discharge of the cell.

OBERLIN COLLEGE, OBERLIN, OHIO,
July 26, 1917.

Farm Weirs. (*U. S. Department of Agriculture*, Farmers' Bulletin No. 313.)—The value of water has increased in the arid lands of the West with the development of the country to a point where there is now a general demand for accurate devices for the measurement of small streams of flowing water. A "weir" is one of the most commonly used devices for this purpose, and the best known are the rectangular, the Cipolletti, and the 90-degree triangular notch types with free fall, sharp chests, and full contractions. Discharge formulæ for these types are given and are so arranged that if the "head" or depth of water flowing over the weir notch is known, the flow by cubic feet per second can be readily ascertained. A table of hydraulic equivalents enables this flow to be changed into miner's inches or statute inches.

Casting Shells in Permanent Moulds. E. A. CUSTER. (*Proceedings of the American Foundrymen's Association*, September 25–28, 1917.)—One of the remarkable changes that the present conflict has brought about is the spectacle of raining upon the enemy an unheard-of number of high-calibre cast-iron shells. There is nothing new in the use of cast-iron projectiles—before this age of steel they

were the sole means of battering down defences and attacking at long range. Some of the reasons why the use of cast-iron shells was abandoned are that the metal has never made a very good record for uniformity, freedom from sponginess and gas-holes; its tensile strength is low, and it lacks toughness. Any of the defects commonly found in cast iron will seriously affect the trajectory and direction of a shell and render it comparatively useless. If one portion is spongy, and hence lighter than the remainder, it will wobble in its flight and its main purpose will be destroyed. The weakening effect of sponginess or blowholes may cause the shell to break under the impulse of discharge and destroy the gun. A forged steel projectile meets all these objections, and for that reason has been universally adopted.

As early as May, 1913, German and Italian munition makers were discussing the manufacture of cast-iron projectiles. In August, 1913, it was reported that shells had been made that were satisfactory, in that they had the proper degree of fragmentation and were strong enough to resist the effect of the propelling charge. These shells were made in iron moulds with iron cores. Their peculiarly destructive effect was later observed in the field, not only in the open, but also against earthworks, and the then prevalent idea that the German forces were using cast-iron shells on account of the scarcity of steel was abandoned.

Target shells have been made of cast-iron for many years, and almost any foundry can make them. The foundry requirements for this work are described in the April, 1917, issue of *The Foundry* by Edgar A. Custer, Jr., and the methods of melting and the care of iron and fuel that must be observed, whether the shells are made in sand or in a permanent mould, are there set forth. Ordinary foundry iron, when properly cast in a permanent mould and when removed at the proper time, has in the resultant casting the same degree of hardness, irrespective of any variation in the chemical constituents, so long as the same size, weight, and shape of casting is made. The time the casting remains in the mould is the determining factor. A casting weighing about 60 pounds remains in the mould 4 or 5 seconds, while a casting of the same general contour weighing 500 pounds will require 25 to 60 seconds before it is safe to lift out.

The low cost and great output per day and effectiveness of cast-iron shells have been so completely recognized that two of the warring nations are using them to an enormous extent. France is casting them in sand, and Germany, from the best information available, is casting them in permanent moulds. A steel forging for a 4.7-inch shell costs over $7 at the present writing, while a casting of the same shell can be made for a little over $2. Furthermore, a liberal saving in labor and machine-tool consumption can be effected. When larger projectiles are made, a larger proportionate saving will follow. When more than 1,000,000 rounds per day are made—and this is a low figure to expect—the difference in cost seems incredible.

ON THE NATURE OF THE ORDINARY GASEOUS ION.*

BY

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THE assumption that the ordinary gaseous ions consisted of clusters of from 6 to 30 molecules surrounding a unit electrical charge was made to explain the fact that the diffusion coefficient of an ion into a gas is from one-fifth to one-tenth as great as the diffusion coefficient of a similar uncharged molecule into the same gas. This assumption has up to the present been accepted as giving the correct explanation of this fact, as well as of the behavior of ions in general. Recent experiments on the mobilities of the ions at low pressures by Wellisch,[1] and on the mobilities of ions in high electric fields by the author,[2] as well as the proof by Franck,[3] Haines,[5] and Franck and Pohl[4] of the existence of "free electrons" as carriers in various gases, have thrown serious doubt upon the correctness of such a theory. An alternative theory was proposed in 1909 by Wellisch[6] and Sutherland[7] which assumed the ions to be single charged molecules. The lowering of the diffusion coefficients was ascribed to an increased drag on the ions in the gas due to their attractive forces on other molecules. In view of the apparent failure of the cluster theory in the light of the newer results it is of importance to study the latter, or "small ion," theory with reference to these phenomena, and to compare the explanations of the various other phenomena which it yields with those of the cluster theory, to see if they are equally satisfactory. It is with this object in view that this paper is written.

It will be generally conceded that modern results all point to the view that atoms of matter are electrical in nature. It is not strange, then, that electrical charges on molecules will exert attractive forces on other neutral molecules. The difference in the two theories as to the nature of the ions lies in the nature of the laws of attraction between the ion and the surrounding molecules. On the cluster theory the force must be very intense when the charge is within one or two molecular radii from the surface

* Communicated by the Author.

of the molecules attracted. It must, however, rapidly diminish to negligible dimensions with increasing distances between the charges and the molecules. In the case of the small ion theory the forces must be comparatively weak even with distances comparable to the molecular diameters between the charges and the molecules. It must never reach such dimensions that the attracted molecules are able to adhere to the surface of the ion under the values of the kinetic energies of impact of gas molecules at ordinary temperatures. The forces must, however, extend with appreciable values over distances large enough to make the apparent size of charged molecules large in comparison to the size of the uncharged molecules. A definite decision as to the validity of one theory to the exclusion of the other would very definitely decide what sort of forces are acting between charges and molecules.

The ions have been most thoroughly studied through the measurement of their mobilities, which may be fairly accurately determined by a number of different methods. The mobility is defined as the velocity of the ion in centimetres per second for an electrical field of strength of one volt per centimetre. This property of the ions is closely connected with the diffusion coefficient to which it is related by means of the equation $U = DP/Ne$, where U is the mobility, D is the diffusion coefficient, P is the pressure, N the number of molecules in a unit volume of the gas, and e the value of the electron.

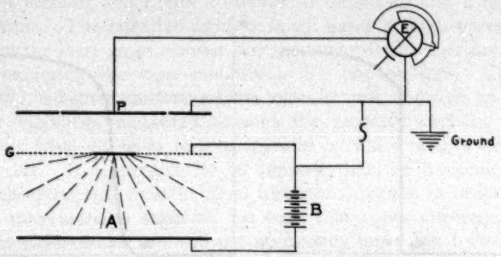
Before * proceeding further with the study of the effect of the various factors influencing the mobilities, it is necessary to make a few comments concerning the methods used in determining mobilities. There are two facts common to all methods of mobility measurement which, as it seems to the author, have not been given the prominence they possibly deserve. The first fact is that in all the usual devices for measuring the mobilities of the ions these mobilities are measured for ions comparatively freshly generated. The importance of this becomes evident when one realizes that under these conditions the mobilities of the ions are determined on ions which may not be in equilibrium with their surroundings. The second fact is that all the measure-

* The explanation of the difference in mobilities of the positive and negative ions and the other phenomena set forth in the following section is still somewhat tentative.

ments give, not the mobilities of single ions, but the mean mobilities of large groups of ions. Thus a small fraction of ions which have not yet reached equilibrium would change the value of the mean appreciably, so that conclusions based on it might be erroneous. As it is to be shown that just such actions taken together with the theory of the small ion might enable one to explain a number of the ion phenomena without recourse to the questionable cluster theory, it is important that these actions be clearly brought out. For the sake of simplicity the Rutherford alternating-current method of determining mobilities as modified by Franck [8] will be used as a typical example.*

In that method the ions generated by the alpha particles of

FIG. 1.



some radio-active substance on the disk ionize the air in the chamber *A*, Fig. 1. The ions to be used are then driven through the meshes of the metal gauze *G* by means of a small accelerating field supplied by the battery *B*. Above *G* is placed a plate *P* which can be connected to an electrometer. The distance to this plate is generally accurately known and kept constant. Between the plate *P* and the gauze the alternating potential is

* This method is used for the sake of simplicity. It looks at first sight as if the Zeleny [4] method which measures the slower ions of a given group would not be subject to the same deviations. It will be seen, on closer scrutiny, that in this case also an appreciable number of ions of changing mobility, due to lack of equilibrium, will influence the curve yielding the critical voltage in a similar manner to that in which these curves are altered in the Rutherford method. The final value of the mobility thus obtained will be about the same.

applied. The frequency of this is in general kept constant, and the potential is varied in making the determinations. The method usually employed is to change the potential of the alternating field and record the values of the ionic currents to the plate P, as shown by electrometer deflections. These currents are then plotted against the potential of the alternating field. If the apparatus be assumed to be ideal, and if the secondary factors to be discussed are assumed to be absent, the curve will take the following form (Fig. 2): Starting with the low potentials, there will be no deflections of the electrometer, or at best small ones, which will be constant, independent of the value of the potential. At a certain critical potential V_0, at which the ions are just

FIG. 2.

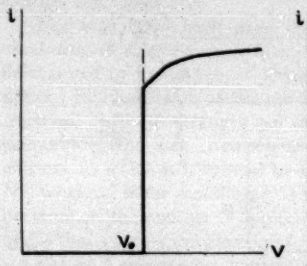
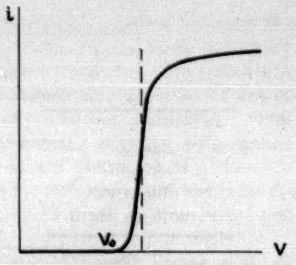


FIG. 3.



able to traverse the distance between the plates in the time of a half period, the current will suddenly rise parallel to the axis of abscissæ. This reaches a certain maximum value, and from then on the current gradually increases with the potential. It is the value of V_0 taken from the curve which, if substituted in a simple formula with the period of alternation of the current and the plate distance, will give the value of the mobility. In practice the ideal case is never realized, for the meshes of the gauze have a finite depth and the ions do not all start from the same level in the meshes. The diffusion of the ions through the gauze would also act to prevent this condition from being realized. The plates are, furthermore, never exactly parallel, and this factor, as well as any irregularity in the field between the gauze and the plate, enhance the deviations. The result is that the

rise of the ion current at V_o, instead of being vertical, becomes inclined to the vertical (Fig. 3). The *point* transitions (*i.e.*, discontinuities) from the horizontal elements of the curve to the vertical element also disappear, and the transition leads to a smooth curve which loses its sharpness more and more the greater these effects. These so-called instrumental errors, when reduced to a minimum, are not of themselves serious, as they act symmetrically. When, however, superposed upon errors due to the agents above mentioned, they may well change the results of the measurements.

The process of ionization consists in the removal of an electron from a neutral molecule, the molecule thus acquiring a resultant positive charge, and on the small ion theory becoming a positive ion. The space below the gauze C is accordingly filled by the ionizing agent with a number of these ions and with free electrons. The negative carriers in all gases at high pressures, except the inert gases, consist, for the most part, of carriers with approximately the same mobility as the positive ions. Consequently, whether clustering takes place or not, in order to have their mobilities measured as ions the negative carriers must change from electrons to ions initially by union with a neutral molecule. It is permissible to suppose that the molecule and the electron must meet in some fortuitous manner in order that they may unite to form an ion such that every encounter between electron and ion will not necessarily mean ion formation. Let it be assumed that it is possible for an electron to traverse a great many mean free paths without uniting to form an ion. Since the electrons start toward the gauze as soon as generated, and since the mobility of the electron is very high, it is possible that a number of the electrons get through the gauze in the free state. Those electrons getting through the gauze will then come under the influence of the alternating field. Some of them will succeed in traversing the space from G to P without uniting with a molecule. The effect of these electrons will be to give an initial current from the plate to the gauze at values of V way below V_o. Most of the electrons penetrating the gauze will combine with molecules before reaching P. The ions formed between G and P will consequently reach P at values of the voltage V *below* V_o, which is necessary for the slow normal ions. Since the number of electrons covering a given distance in the

gas without union follows a probability law, the curve between ion current and voltage from the lower values of V to V_0 will increase according to such a law. Thus the lower corner of the ideal mobility curve would be rounded by this curve (Fig. 4). Such a curve superposed on the curve distorted by the instrumental errors could materially affect the value of V chosen as V_0. The effect of such distortion on V_0 would tend to give too small values for it. Thus the mobilities calculated from such a V_0 would be higher than the *real* mobilities of the negative ions. Since the positive ions have no chance for such a distortion, it is possible that in this action one has an explanation of the difference in mobility of the positive and negative ions. It is to be noted that the gases in which the electrons have been shown to be

FIG. 4.

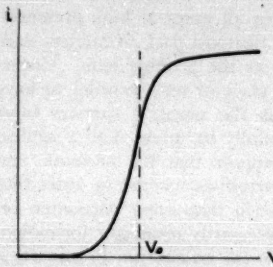
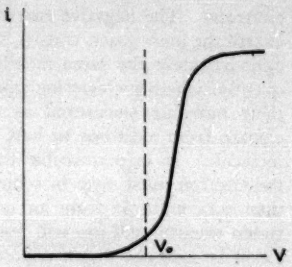


FIG. 5.



free for greater periods of time are the gases that exhibit the greatest differences between the mobilities of the positive and negative ions; *e.g.*, N_2, H_2, air, pure He and Ar, compared to CO_2, CO, NH_3, C_2H_5OH. If such an action taking place to the slight extent which it does is able to produce appreciable changes in the mobilities of the ions in some of the gases at ordinary pressures, it is not in the least surprising that certain gases at low pressures might give quite abnormally high values of the *negative mobility only*. Such mobilities at low pressures were originally taken as evidence for a disintegrating cluster ion.

Again, the following actions might be imagined as taking place. Let it be assumed that the gas contains an easily condensible vapor of a pronounced electronegative character and hav-

ing a high dielectric constant, such, for instance, as alcohol or water vapor. According to Barus,[9] there is evidence that such vapors contain, besides the single molecules, an assortment of groups of molecules, or nucleii, of various sizes. It is on these nucleii that condensation takes place in dust- and ion-free air containing water vapor when eight-fold supersaturation is reached. If such vapors are present in a gas, there will always be a number of such nucleii present per cubic centimetre which will increase as the concentration of the vapor is increased. At low concentration these nucleii would be too few in number to exert much effect. The presence of electronegative molecules alone would tend to decrease the number of *electrons* reaching the gauze in the free state. By an electronegative gas is meant one which shows a tendency to take up negative charges. This is analogous to the use of the term "electronegative" applied to the chemical elements which in chemical combination tend to assume the negative charge where possible. In general, gases which act strongly electronegatively in their chemical reactions will also have a high electron affinity in the molecular gaseous state. In such a gas the encounters between neutral molecules and electrons will more frequently result in ion formation because of the nature of the vapor. The first effect of the presence of such vapors would then be to tend to wipe out the difference in the mobilities between the positive and negative ions by preventing the distortion of the curves through premature negative charges. On increasing the vapor concentration the number of nucleii would increase to such an extent that it would be possible for normal negative or positive ions to encounter appreciable numbers of these between the plate and gauze. The probability of such an encounter is still further increased because of size and high dielectric constants of these nucleii. An ion caught by such a bulky nucleus would never reach the plate P at the value of V_0 for the normal ions. At higher values of V than the true value of V_0, some of these retarded ions will reach the plate and contribute to the current from G to P. The greater V above V_0, the greater the effect of these will become. This abnormal increase of current above V_0 superposed on the instrumental errors will distort the curve in such a manner (*i.e.*, by causing the upper horizontal portion of the curve to slope upwards) that the values chosen for V_0 for the ions will be too

great (Fig. 5). The mobilities of both ions will accordingly appear to decrease with increasing concentrations of the vapors, the values of the negative mobilities decreasing more rapidly than the positive ions—a phenomenon that is actually observed.

Having discussed the effect of certain of the more obscure aspects of the methods of ion measurement, to which reference will repeatedly be made in what follows, one may now turn to the discussion of the ion theories.

1. *Mobility and the Dimensions of the Carrier.*

Except for the case of electrons, the nature of the initial carrier of the charge appears to make little or no difference on the mobility of the carrier. For example, methyl iodide ions in an atmosphere of hydrogen were shown by Wellisch [10] to have the same mobilities as the hydrogen ions. The same holds true for the recoil atoms from radio-active changes, as shown by Rutherford,[11] Franck,[12] and Franck and Meitner.[13] Such results would be predicated on the cluster theory, since the cluster would completely change the original carrier. It would, however, only be possible if a sort of compensating action were supposed to take place between the mass or size of the nucleus and the number of molecules entering into the cluster. This action would assume a decrease of the attracting force on outside molecules of the cluster with increasing dimensions of the nucleus, thus limiting the number of attendant cluster molecules. This assumption does not seem unnatural. On the small ion theory the explanation would be similar, except that in this case the compensating action would take place between the dimensions of the nucleus and the magnitude of the attractive forces on outside molecules, which would *not* involve the formation of a cluster. The increased size of a charged molecule would act to compensate the increase of the mobility due to the decreased drag on outside molecules with a large body to the ion. Accordingly there is no choice between the theories as regards this action.

2. *The Nature of the Surrounding Gas and the Mobilities.*

The action of the nature of the surrounding gas on the mobilities seems to be influenced by several distinct properties of the gas. These, in general, are superposed, and in studying the question it is first necessary to separate them clearly. The prop-

erties of the gas active in this respect are: (1) The molecular weight of the molecules; (2) the dielectric nature of the gas; (3) the electrochemical nature of the gas. It might also be expected that the radii of the gas molecules might be active.

The effect of the electrochemical nature of the gas must be discussed first, as it masks the other factors mentioned. The ratio of the negative to the positive mobilities of the ions in a given gas (*i.e.*, U−/.U+) appears to be greater than unity in all the more electropositive gases. It has never unquestionably been shown beyond the limits of experimental error to be less than unity for any gases.* The assumption will be made at this point that the mobility of the negative ion is never less than that of the positive ion. This means that the normal mobility of ions in a gas is given by the positive ions. It further means that in case the mobilities of the ions differ in the more positive gases, it is the negative ions that for some reasons appear to have abnormally high mobilities. This abnormal mobility of the negative ion in electropositive gases, *i.e.*, gases that tend to lose electrons rather than gain them, has already been explained, in the discussion of the methods of mobility measurements, on the assumption that the electrons, when newly generated, do not unite to form ions with every molecular impact they make. If this view is not accepted, it forces one to assume that the difference of the mobilities is due to the fact that the force of dielectric attraction acting on a group of electropositive molecules is greater for a positive than for a negative charge.† In other words, the dielectric constant varies with the sign of the charge, and this variation is different for different gases. This is an assumption that the writer is loath to make.

* In the results of Wellisch [44] this ratio is about 0.8 for ethyl alcohol vapor, while it is greater than unity in the results of Przibram,[45, 46] and in later results by Wellisch.[46] With this exception, the cases where the ratio of the mobilities is less than unity all lie pretty well within the limits of experimental error. In general the ratios in the electronegative vapors approach unity.

† In a recent brilliant paper [47] Wellisch explains the difference in the mobilities of the positive and the negative ions on the basis of differences in the elasticity of the impacts between negative ions and various neutral molecules. Such differences in the natures of impacts of electrons with different types of molecules were actually observed by Franck and Hertz.[47] It seems to the writer that this is probably the most fruitful explanation of this difference yet proposed.

Turning now to the other factors, one may make use of the assumption that the mobilities of the positive ions are the normal mobilities of the gaseous ions. With this assumption, the variation of the mobilities with the molecular weight of the gases may be studied. Kaufmann [15] pointed out that if the mobilities of the ion in the so-called "permanent gases" (*i.e.*, helium, nitrogen, oxygen, and carbon dioxide) be taken, the mobilities appear to be approximately proportional to the inverse square roots of the molecular weights of the gases. For the vapors and for most other gases this law does not seem to hold, as may be seen from Table I, fifth column, where $U_H/.U_A$ is divided by $(M_A/M_H)^{\frac{1}{2}}$. The resulting figures are not even approximately constant. It was noticed by the writer, in testing this law, that the

TABLE I.

Gas	U* +	$\frac{U_H}{U_A}$	$\left(\frac{M_A}{M_H}\right)^{\frac{1}{2}}$	$\frac{\left(\frac{U_H}{U_A}\right)}{\left(\frac{M_A}{M_H}\right)^{\frac{1}{2}}}$	$(K-1)$	$\frac{(K-1)}{\text{Rel. to } H_2}$	$\frac{(K-1)^{\frac{1}{4}}}{\text{Rel. to } H_2}$	$\frac{\frac{U_H}{U_A}\Big/\left(\frac{M_A}{M_H}\right)^{\frac{1}{2}}}{\text{Rel val. } (K-1)^{\frac{1}{4}}}$	Observer
Hydrogen[15].....	6.02	1	1	1	.000273	1	1	1	Franck.
Helium.....	5.09	1.186	1.42	0.836	.000074	.271	.728	1.15	Franck.
Argon.....	1.37	4.405	4.47	0.986	.000100	.366	.775	1.27	Franck.
Nitrogen.....	1.27	4.755	3.74	1.272	.000590	2.16	1.210	1.05	Franck.
Oxygen.....	1.30	4.64	4.00	1.158	.000540	1.98	1.180	.98	Franck.
Air.....	1.35	4.47	3.87	1.155	.000590	2.16	1.210	.96	Mean.
Ammonia.....	0.74	8.17	3.92	2.795	.007700	28.18	2.310	1.21	Wellisch.
Carbon dioxide...	0.81	7.46	4.69	1.606	.000960	3.51	1.370	1.17	Wellisch (also mean)
Carbon monoxide–	1.10	5.49	3.74	1.466	.000690	2.53	1.260	1.16	Wellisch.
Sulfur dioxide.....	0.44	13.72	5.66	2.425	.009050	32.96	2.400	1.01	Wellisch.
Nitrous oxide.....	0.82	7.37	4.69	1.570	.001070	3.92	1.410	1.11	Wellisch.
Ethyl alcohol.....	0.34	17.75	4.80	3.697	.009400	34.41	2.430	1.52	Wellisch.
Carbon tetrachloride.....	0.30	20.01	8.78	2.280	.004260	15.60	1.900	1.15	Wellisch.
Ethyl chloride....	0.33	18.3	5.67	3.228	.015500	56.80	2.750	1.17	Wellisch.
Ethyl ether.....	0.29	20.8	6.08	3.422	.007420	25.62	2.240	1.53	Wellisch.
Methyl bromide...	0.29	20.8	6.88	3.024	.014600†	53.46	2.710	1.11	Wellisch.
Ethyl formate....	0.30	20.01	6.08	3.292	.008700	31.87	2.380	1.38	Wellisch.
							Mean	1.18	

† Ethyl bromide.

greatest deviations from constancy occurred for gases having the greatest dielectric constants. The value of the dielectric constant for the gases diminished by 1 was then determined for these gases and included in the table. It is seen that if one divides the

* The values of the positive mobilities used in the table are chiefly those of Franck [15] and Wellisch.[6] Those obtained for a large number of vapors by Przibram [16], [14] are not used in this table, since they were determined by a method the results of which are somewhat unreliable. Przibram [16] himself was forced to alter the original values which he published by a considerable factor in a later paper, due to the inaccuracies of the method.

ratio above by the fourth root of the dielectric constant less one relative to hydrogen, one obtains values of the whole ratio that are very nearly constant and equal to unity. This holds over a wide range of compounds. There are a few variations of as much as 30 per cent. from the mean. However, when it is considered that with possible errors of as much as 15 per cent. in the mobilities, and with possible errors of 50 per cent. in the dielectric constants due to the differences in temperature for some of the easily condensible vapors, it is not strange that the agreement is not more perfect. One must conclude, then, that the Kaufmann law holds fairly well, provided the variations of the dielectric constant are allowed for.

One might expect that the mobility would vary as some function of the radius of the molecules in a gas. This does not seem to be the case. In fact, no correlation between various functions of the molecular radii as given by kinetic theory could be found by the writer. This does not seem surprising, as in the case of the uncharged molecules the radius is defined as the mean distance between the molecular centres in collision. What this would amount to in the case of the neutral molecule and the charged ion no one can say. There is no question but that such a radius would depend on the natures of the forces acting on the molecule and the ion; *i.e.*, possibly on the dielectric constant of the molecule, if such a term may be used. The molecular radius is also related in some way to the molecular weight. At any rate, the effect of the radius of the molecules of the gas, or any simple function of this, seems to be absent as an active factor in influencing mobilities.

The relations above give the essential factors of the variation of the mobility with the nature of the gases; *i.e.*, from gas to gas. This variation is superposed on the total abnormal lowering of the diffusion coefficients below that of neutral molecules. Even in the case of positive *helium* ions does one get a positive diffusion coefficient of *considerably lower value* than the diffusion coefficient of neutral atoms of helium. In this extreme case the atoms are small and the value of $(K\text{-}1)$ the lowest of that of any gas. Finally, helium has no valency, is inert chemically, and has apparently very little cohesion. There accordingly must be some agent at work which causes the *initial lowering* for *all atoms* and *molecules*. The effect of the other factors would be

superposed on this. If this superposed effect be removed, an initial lowering which is the same for all atoms and molecules should appear. This becomes clear in Table II. In this table the diffusion coefficients are given as calculated from the formula $D = 300\ U\ P/Ne$, or very nearly $D = .0236\ U$. Besides this, the table includes the values of the diffusion coefficients of the *neutral molecules* as actually determined for some gases into gases of equal molecular weight. In one case the diffusion coefficient is estimated for these molecules. It may be seen that the values of the ratio of the diffusion coefficients for the molecules to that of the ions range from four to thirteen. It

TABLE II.

Gas diffusing	Gas diffused into	D molecules	U +	D + for ions	D ions actually measured	Relative D molecules / D ions	(K-1) ¼ relative to H_2	D mols. / D ions (K-1) relative to H_2
Argon	Helium	.706	5.09	1.20	....	5.88 **	.0728	8.10 **
H_2	Nitrogen	.739	6.02	.143	.123	5.16 6.01	....	5.16 6.01
Air	Oxygen	.178	1.35	.0319	.028	5.58 6.36	1.18	4.73 5.38
O_2	N_2	.171	1.27	.0299	.025	5.72 6.85	1.21	4.73 5.68
CO_2	N_2O	(1.5–1.0)	.82	.0193	.*023	0.772 6.52	1.37§ / 1.41	5.73 4.76 / 5.47 4.73
CO_2	CO	1.31	.81	.0193	....	6.80	1.37	4.96 ....
C_2H_5OH	CO_2	.0693	.34	.00805	....	8.50 ...	2.43	3.49 ....
Air	Ethyl acetate	.093	.30†	.0071	....	13.1 ...	2.38	5.51 ....
H_2O	Air	.246	1.35	.0319	....	7.72 ...	1.18	6.53 ....
NH_3	NH_3	.190‡	.74	.0174	....	10.9 ...	2.31	4.72 ....
							Mean	5.3

* For CO_2 into CO_2.
† For ethyl formate.
‡ Estimated.
§ For CO_2 and also for N_2O.
**Values from actual observed values of D ions.

can be further seen that here, as before, the highest values of these ratios lie with the gases that have the highest values of $(K\text{-}1)$. If one divides the relative values of the ratios by the fourth root of $(K\text{-}1)$, as was done for the mobilities, one finds that this ratio is reduced to a fairly constant value; *i.e.*, about 5.3. The greater variations from constancy observed here are due to the fact that the diffusion coefficients of the molecules into molecules of the same kind could not be used. Approximations had to be made, and it was assumed that, for instance, the value of D for C_2H_5OH into CO_2 was the same as for C_2H_5OH into C_2H_5OH vapor, a wild assumption at best. In the table allowance was made, as far as possible, for the variation in molecular

weight, but no allowance was made for the shape of the molecules; *i.e.*, whether they were di- tri-, or polyatomic. It can be concluded from this that an initial lowering of about fivefold in the coefficients may really exist.

The Kaufmann law could be expected to hold equally well on either theory. The action of the value of K-1 in influencing mobilities would also be expected on either theory. The fact that it is the fourth root of K-1 that enters into the Kaufmann law as a correction seems to favor the small ion theory to a slight extent. Nearly all of the cluster theories contain the value of K-1 to the first power as a factor. This, as will be seen later if coupled with an inverse fifth power law of force between the molecules and charges, inevitably leads to a very stable cluster. Consequently the smaller factor obtained above might indicate the existence of a weaker law of force. The general abnormal lowering of the diffusion coefficients of the ions is the original phenomenon which called for an explanation by means of one or the other of the theories. The absence of any dependence of the mobilities on molecular diameters as determined by kinetic theory would have no meaning. The difference between the positive and the negative mobilities in certain gases offers no difficulty to either theory on the explanation given above, unless the reluctance of electrons to unite with molecules to form an ion at first encounter be considered an argument against the cluster theory (see later).

3. *Gaseous Mixtures.*

The influence of mixtures of gases on the mobilities has been but very little studied, with the result that the explanation of the behavior of the ions in mixtures has not lent itself to treatment by any of the mathematical theories yet deduced. The mobilities in mixtures seem to show three different types of deviation from the mobilities in pure gases. Franck and Pohl [3, 4] found that the mobilities of the negative carriers in pure helium and argon were of the order of magnitude of 200 or more. This high mobility of the negative carriers was explained by the assumption that they were electrons which were not attached to atoms. They further found that when small traces of the more electronegative gases were added to the inert gases the mobilities of the negative carriers rapidly fell to the values ob-

served for the positive ions. This may be explained by the assumption that the electrons which were not able to attach to the molecules of the inert gases promptly attached themselves to the molecules of the impurities added, thus forming negative carriers of the dimensions of the normal ions. The greater the concentrations of the impurities, the greater the number of ionic negative carriers formed, and the more nearly normal the negative mobilities will appear.

As an example of the second sort of change produced in the mobilities of the ions on mixing the gases, one may quote the following results taken from a paper by Wellisch [10] as being typical: SO_2 and O_2 were mixed such that the partial pressures were 131 mm. and 629 mm. respectively. The mobilities were measured in this mixture and found to be $u+=0.72$ and $u-=0.76$, while the mobilities in pure SO_2 were $u+=0.44$ and $u-=0.44$, and in O_2 were $u+=1.36$ and $u-=1.78$. In other words, the mobilities seem to take on values intermediate between the mobilities in the pure gases. The lowering of the mobility is greater than would be expected on the assumption that the mobilities followed the simple law of mixtures. No data have been taken for a variety of different concentrations of the same two gases, and so no accurate conclusions can be drawn as to the relations between mobilities in mixtures of gases and the relative concentrations.

The abnormal changes in the mobilities of the ions caused by the addition of small quantities of certain of the very electronegative vapors exhibit a third effect of mixing the gases on mobilities. A striking example of this effect may be seen in the following results.[10] The mobilities were measured in air at atmospheric pressure with an added pressure of

	$U+$	$U-$
6 mm. C_2H_5Br gave	1.37	1.80
6 mm. CH_3I gave	1.37	1.80
10 mm. C_2H_5OH gave	0.91	1.10
9 mm. C_4H_8O gave	1.15	1.37
..... nothing gave	1.37	1.80

These substances are all vapors. The lower two which exert the abnormal effect on the mobilities are substances of pronounced electronegative character that have high dielectric constants in the liquid state and that are also highly associated in that state. Water vapor also belongs to this class.

The first class of lowering discussed is independent of any theory of the ions. On either theory the electron must first add onto at least one molecule before it becomes an ion, which is all that is needed to explain the effects observed. The discussion of the existence of unattached electrons in general will be left to a later topic. The normal change of the mobilities due to mixing two gases is equally well explained by either theory. In the case of the cluster theory, either the size and the composition of the ion may change with changing relative concentrations, or the composition of the cluster may stay fixed and the effect of changing the mixture could be caused by a change in the properties of the surrounding gas molecules which do not enter into the cluster. It seems quite likely that both of these effects are of importance, for the latter effect alone might lead one to expect the simple law of mixtures to hold. On the small ion theory the effect of an altered cluster is substituted by a change in drag on the small ion by changes in the natures of the surrounding gas molecules. The third type of change in mobilities caused by small traces of certain of the negative vapors can be explained by assuming that, due to the powerful associative tendencies of these vapors, the Barus nucleii are present in appreciable quantities. These would have the effect on the mobilities due to the peculiarities of the methods of measurement which have been already discussed. This explanation applies equally well to the cluster and the small ion theories. Aside from this explanation, the cluster theory attempts to explain this effect by assuming the formation of abnormally large clusters with such vapors of high dielectric constants and strong electronegative properties. The cluster theory would expect the presence of only enough of the negative molecules to form the large clusters. The small ion theory would demand concentrations of the vapor sufficient to produce the requisite number of Barus nucleii. No decisive differentiation between the theories can be made in this field until quantitative determinations have been made on the lowering produced by different percentages of the negative vapors. The net result of this discussion of the effect of mixtures has been to show that the small ion theory is capable of explaining these effects about as well as the cluster theory can. Under these circumstances these phenomena may not be urged as arguments against a small ion theory.

4. *Condensation Experiments.*

The phenomenon of the condensation of supersaturated vapors on ions or nucleii is very closely allied to the action of certain vapors on the mobilities. C. T. R. Wilson [16] found that ions present in dust-free gases saturated with water vapor, alcohol vapor, etc., would, if the gas were adiabatically expanded, cause the vapor to condense on them and to form a cloud of drops even when the expansion was well below the amount sufficient to cause such condensation in ion-free air. In the case of water, the negative ions became condensation centres on an expansion to 1.25 the former volume, the positive ions on an expansion to 1.34 the former volume. With other gases, the positive ions act more readily than the negative ions. The values given above for water correspond to a four-fold supersaturation in the case of the negative ions. In dust-free air on eight-fold supersaturation, the condensation takes place in the absence of ions.

J. J. Thomson [18] worked out the energy relations involved in the formation of drops for different conditions of supersaturations as determined by the forces of condensation, evaporation, surface tension, and electric attractions. A drop once formed under given conditions of supersaturation will not necessarily grow to a larger drop. This is due to the action of surface tension in increasing the vapor tension. An electric charge placed on a drop that might even be evaporating under the conditions in which it is placed when uncharged would preserve the drop and aid it in passing the critical stage in its growth to a visible cloud particle. The manner in which the drop acquires its charge has no influence on this action; so that it makes no difference whether the drop grew from a cluster ion or became charged through picking up an ion after being formed. The small ion theory is then in perfect accord with the condensing action of ions.

The cluster theory, on the other hand, demands that some of the drops be formed by the ions which pass through the intermediate stages between ion and drop, such as those that the Langevin ions were supposed to represent. Accordingly, the existence of the Langevin ions was initially used as a first-class argument for the cluster theory. On this theory the normal cluster ion in supersaturated gases was supposed to grow through the two classes of the so-called Langevin, or slow, ions and to

finally become a regular drop. This has since been shown to be wrong by Pollock.[17] Pollock comes to the conclusion that the Langevin ions consist in all cases of solid particles of minute dimensions surrounded by a mantle of water vapor or liquid water and carrying an electric charge. This is strikingly borne out by the fact that these ions never develop in dust-free air. The charge on these ions assumes only a secondary rôle, leading to the electrical detection of the particles, and was probably acquired in a manner similar to that by which the oil drops of Millikan acquire their charge. Other than the Langevin ions, no intermediate ions have ever been detected. It is therefore evident that, unless the existence of the intermediate ions is so transient that they cannot be detected, the cluster theory leads to conclusions that are not in agreement with the facts.

The difference in condensing power of the positive and the negative ions in different gases needs some explanation. The substances exhibiting these properties are distinctly electrically polar in nature. If a droplet of one of these substances should pick up an electric charge, one would expect the charge to go to the centre of the droplet. The polar elements in the drop would arrange themselves so that the charged parts of the molecules directed outwards would be of the same sign as the charge picked up. It is to be expected that in a vapor having strong electronegative tendencies (*i.e.*, strong tendencies to acquire negative electrical charges) the molecules would more readily attach to a surface of predominating negative sign than one of the opposite sign. Accordingly, in the case of water vapor, it is not surprising that the droplets should grow more rapidly if they have negative charges than if they have positive charges. The cloud formation then takes place more easily on the negative than on the positive ions. For alcohol vapor, which appears to be less negative, the reverse seems to be true. This suggestion of the mechanism of condensation is independent of the theory assumed. It enables one to avoid explaining the action as due to a difference of dielectric constant of the vapor molecules for charges of opposite sign by substituting for this the assumption that the action depends on the electrical nature of the forces of association (*i.e.*, chemical forces) where preferences for charges of different sign are known to exist.

5. *Temperature Coefficient of Mobility.*

The temperature coefficient of mobility has been very incompletely studied. Phillips [19] and also Kovarick [20] determined the mobilities of the ions in air at temperatures ranging from 84.5° to 698° absolute with varying densities, correcting their results to reduce them to constant densities. Above 300° Abs. there was no change appreciable with temperature. Below that temperature the mobilities seemed to decrease somewhat with the temperature, this decrease being much greater in the results of Kovarick than of Phillips. Erikson [21] reported measurements on mobilities, using a method which allowed the density to be kept constant. The latter measurements are but few in number and cover temperatures between 80° and 300° absolute. The mobilities were found to be perfectly constant down to the lowest temperature, where a lowering of 10 per cent. was found. Both Phillips and Erikson reported that the difference in the mobilities of the positive and the negative ions seemed to disappear at the lower temperatures. Kovarick worked only on negative ions.

The cluster theory explains the independence of mobility and temperature as due to the fact that as the temperature goes down the size of the cluster increases; this increase, however, is balanced by the decrease of the viscosity of the gas with the decrease in temperature. If the results of Kovarick be accepted as correct, the increase in the size of the cluster proceeds more rapidly than the decrease of viscosity of the gas. The effect is contradicted to a large extent by the results of both Erikson and Phillips, so that it seems questionable. Sutherland,[7] using methods similar to those he used in calculating the change of gaseous viscosity with temperature, developed a mathematical theory of the variation of mobilities with temperature based on the small ion concept. This theory reproduced the variations of mobility with temperature observed by Phillips with remarkable accuracy. The Sutherland [7] theory of the small ion here seems to have a distinct advantage over the cluster theory, inasmuch as it can actually predict the behavior of the ions with temperature quantitatively.

The disappearance of the difference of the positive and negative mobilities at the lower temperatures may be accounted for by ascribing the difference of the positive and negative mobilities to the cause already assumed. At low temperatures the increased

densities of the gases and the slower heat motions of the molecules greatly increase the probabilities of union between the electrons and molecules to form negative ions. In this way the mobilities measured for the negative ions will approach those of the positive ions. This explanation is independent of either theory.

6. *Mobilities at High Temperatures.*

The mobilities of the ions at the higher temperatures, ranging from 450° to 1900° C., have chiefly been measured in flames. Since, in this case, chemical reactions play such tremendous rôles and the numbers of the charged particles are very great, the results become very complicated. The complexity of conditions further has resulted in seriously conflicting results being obtained by the different observers. It therefore seems inadvisable to attempt to judge the theories on the basis of any of these results.

7. *Pressure Coefficient of Mobility.*

The mobility has been found to vary inversely with the pressure in air over a very large range of pressure extending from 100 atmospheres down to 1/10 atmosphere for the negative ions, and down to 1/1000 atmosphere for the positive ions.[22, 23, 20, 6, 1] At the higher end of the pressure range the mobilities are found to decrease slightly less rapidly than the inverse pressure law would lead one to expect. At 1/10 atmosphere in the case of the negative ions all observers agree in concluding that the mobility of the negative ion in air (other gases at other pressures) appears to increase abnormally rapidly.[24, 20, 25] The positive ions have been observed to do this only according to the results of one observer,[26] which have been called into question by the more recent and careful experiments of Wellisch.[1] The results of Wellisch showed not only that the positive ions have normal mobilities down to the lowest pressures ever worked with, but that the abnormal increase in the mobilities with decreasing pressure for the negative ions was only *apparent*. His results showed that in his mobility measurements there were large numbers of unattached electrons present, at all pressures below ten centimetres of mercury, that reached the plate of his measuring apparatus. In the measurements which he made, however, these electrons did not completely mask the point where the normal ions began to appear. Besides the electrons, whose number apparently in-

creased as the pressures were reduced, Wellisch found that there were negative ions with mobilities regularly inversely proportional to the pressure down to the lowest pressures at which he could make measurements. In the analysis of the methods of making mobility determinations it was shown that a small number of electrons that did not unite to form ions before reaching the gauze could raise the apparent values of the negative mobilities. As pressures are decreased, the chance of an electron uniting with a molecule is decreased; for the free paths of the electrons and molecules vary inversely with the pressure, while the dimensions of the apparatus are sensibly unchanged. The number of electrons passing through the gauze is therefore rapidly increased as the pressure decreases. In some of the experiments of Wellisch at the lower pressures nearly as many as 50 per cent. of the carriers between the plate and gauze were electrons. In measurements where the electrons are not detected as carriers the effect of their presence must have altered the shapes of the curves in such a way as to give absolutely fictitious and high values for the mobilities. Such was the case with all of the earlier observers at low pressures with the negative ions. The mobilities of the ions are all, therefore, strictly inversely proportional to pressures up to 100 atmospheres.

Before the cause of the abnormally low mobilities of the negative ions was shown by the work of Wellisch, the assumption of the labile cluster ion which began to shed some of its molecules at pressures of about 10 cm. of Hg in air was essential. This excuse for assuming a cluster ion is now obsolete. The assumption of a cluster theory is, however, still in perfect harmony with the behavior of the ions as regards the inverse pressure law. The small ion theory is also in perfect accord with these results, since the abnormal negative mobilities at low pressures have been explained. The abnormal decrease of the mobilities at the high end of the pressure range is not explained on either theory, though it is doubtless a real phenomenon, having been observed by all observers, Dempster,[27] Kovarick,[29] and McLennan,[28] at these pressures.

8. *Mobilities and the Value of the Ratio X/p.*

A crucial test which should enable one to judge between the two theories lies in the behavior of the ions when subjected to

very high velocities. The energy acquired by an ion due to an electric field depends on the magnitude of the field acting on the ion and the time over which it acts. It therefore follows that the energy will be the greater, the greater the product of field strength and mean free path of the ion becomes. It will be more convenient to substitute for this product the value of a ratio X/p, (which is proportional to it) where X is the field strength in volts per centimetre and p is the pressure in millimetres of mercury. On a cluster theory it would be expected that an ion would shed some of its attendant cluster of molecules before it acquires sufficient energy to ionize other molecules by impact; *i.e.*, before the conditions for initiation of ionization by collision set in. Such a shedding would result in an abnormally rapid increase of the mobility with an increase in the value of the ratio X/p. The small ion theory would not predict such a result, the mobility remaining essentially normal.

The apparent abnormally rapid increase of the mobilities of the negative ions as the pressure was reduced was formerly ascribed to the above type of shattering of the cluster. Townsend [25] fixes the value of X/p for the shattering of the negative cluster at about 0.2 or less. However, in light of the experiments of Wellisch, this explanation of the negative mobilities at low pressures is now no longer valid.

Up to 1915 no determinations of mobilities at high values of X/p had been made at higher pressures except those resulting from the study of the discharge of points. Chattock [30] and Tyndall [31] found normal mobilities of the ions in fields up to strength of 3000 volts per centimetre; *i.e.*, values of $X/p = 4$. Later measurements by Tyndall [32] indicated a possibility of abnormal increases of mobilities with increasing ionic currents. In a letter to the writer, Professor Tyndall states that he now "has reason to doubt the accuracy of those results" so far as this effect was concerned. Franck [33] and also Moore,[34] in fields of about 10,000 volts per centimetre, apparently obtained abnormal mobilities for both ions. They were working near the threshold of glow discharge where the uniformity of their fields as well as the value of their field strengths are to be questioned. In 1916 the writer,[2] using a modification of the Rutherford alternating-current method for determining mobilities and using high-frequency oscillations of the Chaffee arc, determined the mobilities of the

ions in dry air at fields as high as 12,000 volts per centimetre; *i.e.*, $X/p = 18$. He found only normal values of the mobilities, the negative ions in no case showing a tendency to increase relatively to those of the positive ions. Ratner,[35] in a still later paper, finds perfectly normal mobilities of the positive ions up to the point of the glow discharge, using a modification of the Chattock and Tyndall[30,31] method. The negative ion in his results appears to acquire abnormally high mobilities in fields of 1800 (volt per cm.) in air at atmospheric pressure; *i.e.*, $X/p = 2.4$. He also detects large numbers of electrons acting as carriers by this method. The method used consists in accelerating ions generated by a radioactive substance or an incandescent wire by means of an electric field, and measuring the wind-pressure produced. This pressure is measured by the deflection of a light vane which can give only the relative values of the pressures, but not absolute values. In order to calibrate the vane to give the absolute values of the pressures, mobility measurements were made on ions in normal fields, where they are known, and the pressures computed from these results. In the case of the negative ions, Ratner's method encounters difficulties through the fact that the measurements are made on very freshly generated carriers, among which, according to him, are appreciable numbers of unattached electrons. The method which he uses assumes that if the ions move with *uniform* velocities the pressure due to the drag of the ions on the gas molecules is equal to drX, where d is the distance between the plates, r is the density of electrification of one sign, and X is the field strength. Since the electrons combine to form the ions all along their paths through the field, the condition of uniform velocity is not fulfilled. As a result of such an action, it is not surprising that Ratner obtained abnormally high mobilities for the negative ions. Chattock and Tyndall got no such effect at nearly twice the values of X/p which he used on the negative ions, though they used essentially the same method. In their case the carriers were generated by the point discharge. It is quite possible that such carriers are, at the lower field strengths in point discharge, generated as ions directly, and that consequently there were but few electrons present in the determinations.

The conclusion to be drawn is that the ions show *no* tendency to take on abnormal values of the mobilities for any values of the ratio of X/p up to the point where ionization by impact begins.

These results speak unmistakably against the labile cluster theory. Furthermore, if an apparent breaking up of a negative cluster did appear, as is assumed by Ratner, the cluster theory would encounter considerable difficulty in explaining why it is that the positive cluster is so many times more stable than the negative cluster.

9. *Free Electrons.*

It was early noticed by Franck and Pohl [3, 4] that the negative carriers in very pure samples of He, Ar, and N_2 had remarkably high mobilities. These were correctly explained on the assumption that negative carriers in the gases were in part free electrons. Recently Haines [5] and also Wellisch [1] have shown that a small fraction of the carriers in hydrogen and air are also of this nature. In air the number is too small to detect at ordinary pressures, but they become appreciable at about 10 cm., according to Wellisch. The presence of electrons as negative carriers, as well as normal negative ions in most of the common gases, may be explained in two ways. Wellisch [1, 46] assumes that the electrons exist *permanently* in those gases as carriers. The percentage of carriers of this type that exist in a gas depends on the pressure and the nature of the gas. To explain this fact, Wellisch assumes that in order for an electron to form an ion by union with a neutral molecule the electron requires a certain threshold value of kinetic energy. This the electron acquires at the instant of ionization from the ionizing source; *e.g.*, X-rays, or alpha particles. The expulsion of the electron leaves the parent molecules with a residual positive charge. As the electron recedes from the molecule, some of its kinetic energy is converted into potential energy of separation. This conversion of the energy might become sufficient to lower the kinetic energy of the electron below the threshold value for ion formation. This would be more likely to occur, the smaller the initial energy of liberation of the electron the longer the mean free path, and the higher the value of the kinetic energy required. The latter would depend on the electrochemical nature of the gas. Therefore, the electrons which recede too far from the parent molecules before encountering neutral molecules will be unable to form ions and will be the free electrons of Wellisch. This theory, though very pretty, is open to one objection. The experimental curves obtained by

both Wellisch and Ratner indicate that union between electrons and molecules takes place all along the space between the plates; *i.e.*, apparently intermediate ions of all mobilities between electrons and ions are present. On the above view of Wellisch the curves should appear as if they were composed entirely of two groups of carriers present in very definite ratios from the start, which is obviously not the case. The theory of Wellisch is further open to test, for with different ionizing agents the electrons should receive different amounts of energy at the start. As a result the pressures at which the free electrons just begin to appear in a given gas should depend to some extent on the ionizing source.

J. J. Thomson [36] recently attempted to explain the existence of the electronic carriers as follows: He assumed that an electron and a molecule did not necessarily form an ion on every encounter, an assumption which seems plausible, as it might be expected that it would be necessary for an electron to strike certain definite localities in a molecule before it could be incorporated in the form of an ion. He further assumed that the chance that a single collision between the two would result in ion formation was $1/n$, where n is a number (possibly very large) characteristic of the gas only. On the basis of these assumptions he mathematically deduces the consequences which would be expected if the mobility of the ions could be measured ideally by a simplified method. In practice, if n were great or the mean free path were long (*i.e.*, pressure low), it would be expected that the electrons might traverse several centimetres in the gas without union to form ions. This is the more likely as the mean free path of the electron is supposed to be quite long. The mobilities of negative ions determined in a gas of electropositive properties (*e.g.*, where n is large and at low pressures) would then apparently be abnormally high, as previously explained, while considerable numbers of free electrons would be detected between the plates.

Haines reported in the papers in which he shows the existence of the electronic carriers in hydrogen that, besides these and the normal negative ions, he finds evidences of groups of ions of intermediate mobilities. These he at once ascribes to clusters of different compositions. The curves which give this evidence show marked bends at potentials lower than those required to detect the normal negative ions, an effect that is totally absent in the

curves of Wellisch and of Ratner. The positive ions appear to behave perfectly normally. The writer feels inclined to seek for the cause of these results in peculiarities of the method of determination, in view of the contradictions above mentioned.* In his determinations Haines used a distance between the plate and the gauze in the Rutherford alternating-current method varying from four to ten centimetres. The plates and gauze are closely surrounded by the glass insulating walls of the measuring chamber used. These glass walls, from the writer's own experience, may become highly statically charged through the diffusion of the ions to them. In the case of the negative ions, where numbers of rapidly moving free electrons are able to migrate to these walls, this effect could become appreciable. Further, in Haines's earlier experiments a stream of gas was constantly passing through his gauze. These three factors would all tend to distort the field between the plate and the gauze, making it far from uniform, and it is possible that this lack of uniformity of the field caused the distortion of the curves reported. In this connection it might be pointed out that Todd [26] in his mobility measurements used plate distances of ten centimetres. He was later forced to repeat his experiments, using a series of annular disks connected to a potentiometer in his field in order to keep his field uniform. This proceeding considerably modified his later results.

From the foregoing it seems that the explanation offered by J. J. Thomson of the existence of the electron as a carrier in the mobility determinations is the best adapted for use, particularly as it leads to considerations that are included in the discussion of the methods of mobility measurement. With this view of the existence of the free electrons, it seems wrong to assume that a comparatively stable cluster of neutral molecules surrounding a negative electron could exist in the gases where the electron shows so much reluctance at uniting with a single molecule. The comparatively weak forces appearing to exist between free electrons and molecules speak more in favor of a small ion theory. It must consequently be concluded that in this case the small ion theory again has a distinct advantage over the cluster theory.

* Recently Mr. K. L. Yen, at the University of Chicago, has made some determinations of the mobility of the negative ions in a number of gases, in which, though both normal negative ions and free electrons were found, no traces of intermediate negative ions could be noticed. The results will, I believe, be published shortly.

10. *Conclusion.*

In reviewing the preceding considerations one is forced to conclude that the concept of a *labile* cluster ion is not well adapted to explain the properties of the gas ions, since it encounters serious difficulties in explaining (1) the independence of the mobilities and the value of the ratio X/p, (2) the reluctance of electrons to unite to form ions with ordinary molecules, and (3) the absence of intermediate types of ions to be expected from the growth of an ion to a drop in the condensation experiments. In most other respects the explanations furnished by the labile cluster theory seem entirely adequate to account for the phenomena, so far as one is able to judge from the meagre experimental data available. With the exclusion of the *labile* cluster theory it is still possible to explain the initial five-fold lowering of the mobility coefficients by assuming the formation of a very *stable* cluster ion. This must be an extremely stable cluster that is capable of withstanding the action of fields with high values of X/p, and which must depend for its other properties on actions similar to those assumed for the small ions. Unfortunately the second objection urged against the *labile* cluster theory becomes a still more serious objection to this theory.

One is accordingly forced to turn to the small ion theory in some form or other, as this *apparently has no serious contradictions* in the light of foregoing analysis. Some nine or ten mathematical theories, giving as many different equations showing the relationship between the mobilities of the ions and the various molecular constants, have been proposed by Riecke,[37] Langevin,[23, 43] Lenard,[38] Thomson,[39] Reinganum,[40] Sutherland,[7] Wellisch,[6] Przibram,[41] and Kleemann.[42] These theories have been deduced starting from various assumptions based on kinetic theory of gases. All of these theories, with the exception of that of Wellisch, provided one excludes those containing indeterminate constants, lead to equations which, when evaluated in terms of the molecular constants, yield values of the mobilities from five to ten times too high. These defects of the theory are at once ascribed to the existence of a cluster whose existence had been ignored in setting up the equations by the men who incline to the cluster theory. In the case of the advocates of a small ion theory the discrepancy between the mobilities expected from the theory and the actual observed mobilities is ascribed to an increased drag

produced on the ions by the action of their charge on the neutral molecules, a factor which had been omitted in the initial deduction. In either case, in order to make the theories yield correct results, an arbitrary numerical factor is introduced into the equation, so that the mobilities obtained from it are of the correct order of magnitude.

The small ion theory of Wellisch [6] is the only one which starts from accepted theoretical considerations, and without resort to any arbitrary numerical factors yields correct values for the mobilities. The theory, unfortunately, has one serious defect. A term $R=(K-1)e^2/8\pi\ ns^4$ is introduced into the equation, as well as into most of the cluster theory equations above mentioned, which is supposed to be related to the apparent increase in size of the ion due to its charge. R is the potential of the ion of charge e on a neutral molecule of dielectric constant K (if such a term may be used) at a distance s. K is taken as the value of the dielectric constant of the gas in bulk. The use of this factor R in a small ion theory is *not correct*. To the writer's mind it seems equally questionable whether it is legitimate to use it in any ion theory, for the reasons which follow:

1. An atom is now pictured as a rather diffuse system of electrons surrounding a highly charged minute positive nucleus. If a single unit charge concentrated in an electron be placed within a distance comparable to the diameter of such a neutral atom or molecule, it seems absurd to assume the potential energy of this system would be the same as that for a mass of many molecules in bulk. It is consequently very questionable whether it is proper under any such circumstances to use this equation at all.

2. This law, furthermore, leads to the formation of a very stable cluster ion in air if the proper values are introduced for the various quantities. This may be seen from the computations below, where it becomes evident that a temperature of 1190° absolute, or a field of over 16,080 volts per centimetre at 760 centimetres Hg pressure, is required to cause this ion to begin to disintegrate, assuming a mean free path of the ions equal to that for normal gas molecules. This ion cluster, at least to within a molecular diameter beyond that of the central molecule, would therefore have a stability exceeding that of some chemical compounds. A term such as R introduced into the *small ion theory* of

Wellisch would make it *meaningless*, for the term leads inevitably to a cluster formation.

For a cluster in which the factor R appears:

$\frac{R}{K.E.}$ at 0° and 760 mm. *Hg* pressure of air, is,

$$\frac{R}{K.E.} = \frac{(K-1)e}{4\pi n m v^2 s^4} = \frac{(K-1)e^3}{12\pi P s^4} = \frac{(.00058)(4.8\times10^{-10})^2}{12\times3.1\times1.01\times10^6(3\times10^{-8})^4} = 4.37$$

$K.E.$ is kinetic energy of surrounding gas molecules.
P = atmospheric pressure in dynes.

i.e., potential energy of cluster is greater than the kinetic energy of the surrounding gas molecules. The ion is therefore stable.

The temperature for which $\frac{R}{K.E.}$ equals unity, *i.e.*, the break-up temperature of the ions, is $4.37\times273° = 1190°$ Absolute.

The value of the electric field (X) necessary to shatter the ions if the mean free path is 9.95×10^{-6} centimetres is

$$\frac{R}{K.E.} = 1 = \frac{R}{\frac{1}{2}mv^2} = \frac{R}{Xe\lambda} = \frac{(K-1)e^2}{8\pi X n\lambda e s^4} \quad \text{where } \lambda = \text{mean free path of molecules of air.}$$

$$X = \frac{e(K-1)}{8\pi n s^4\lambda} = \frac{5.8\times10^{-4}\times4.8\times10^{-10}}{8\times3.1\times2.6\times10^{19}\times9.9\times10^{-6}(3\times10^{-8})^4}$$

$$= 16{,}080 \text{ volts per cm.}$$

or a value of $X/p = 21.2$, *i.e.*, assuming λ for gas ions to be the same as that of molecules.

The one small ion theory that is free from such an assumption is that of Sutherland. This theory, however, is one of those which is forced to include an arbitrary constant in order to make it yield the true mobilities of the ions. It is the theory which successfully yields the variation of mobility with temperature found by Phillips. The theory also predicts the Kaufmann law between mobilities and the molecular weights of the gas in which the ion moves. As this theory is a small ion theory, as no serious objections may be raised against it, as it appears to predict some of the more fundamental laws of ionic behavior quite well, and, finally, as it is well adapted to expansion as the knowledge of the structure of molecules advances, it seems to the writer to be the most successful ion theory yet proposed.

In conclusion the writer desires to express his sincere thanks to Prof. R. A. Millikan for his valuable criticism of this paper and his kind interest in it. The writer's thanks are also due to Dr. N. E. Dorsey for his kind advice. The writer desires to

acknowledge his indebtedness to the excellent review of the field of mobility measurements and bibliography on mobilities of the ions prior to 1912 included in a paper by Franck,[14] entitled "Bericht über Ionenbeweglichkeit."

NATIONAL BUREAU OF STANDARDS,
Washington, D. C.,
June 12, 1917.

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Electrolytic Pickling Process and Its Effect on the Physical Properties of Iron and Steel. J. COULSON. (*Proceedings of the American Electrochemical Society*, October 3–6, 1917.)—Brittleness of steel springs resulting from acid pickling and electroplating is a well-known phenomenon. Tempered springs which are pickled even for a few seconds in an acid bath snap when subjected to strain. Such springs, however, can be electrolytically pickled without destroying their resiliency. It is known that metals absorb gases and that the amount absorbed depends upon the nature of the gas, the condition and character of the metal, and the surrounding medium. These absorbed gases appear to have an important influence on the behavior of iron, steel, and certain alloys. Electrolytic iron is extremely brittle, due principally to occluded hydrogen, and there appears no doubt that the brittleness of steel springs after pickling is caused by the absorption of hydrogen during the ordinary pickling process. The effect is still more pronounced if the springs are made the cathode in an acidulated electrolyte.

To determine the embrittling effect of adsorbed hydrogen upon steel pickled in different ways, samples of steel wire were pickled chemically by simple dipping in acid, also by electrolytic pickling, using them as cathodes or as anodes. Oscillation tests on the original wires, sand blasted, and three sets treated as described, showed the chemically cleaned and the cathodically cleaned to be very brittle, while the anodically cleaned had the strength of the original samples. Similar tests were aso made with drill-rod steel, hot-rolled Bessemer, and cold rolled steel, after which mechanical tests were made as to strength, elongation, and reduction of area. The chemically and cathodically cleaned specimens again showed greater brittleness, which was most marked with the high-carbon steels and less marked with the soft steel.

PHYSICS OF THE AIR.*

BY

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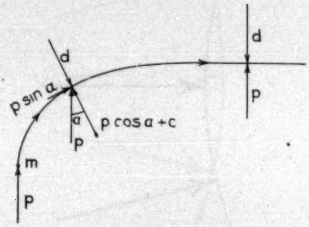
CHAPTER VIII (*Continued*).

Automatic Adjustment of Winds in Direction and Velocity.—In discussing the more extensive winds it is convenient to consider the earth as stationary and the air as moving over it without friction under the influence of three distinct horizontal forces: (1) The deflective force, due to the earth's rotation; (2) the horizontal component of the centrifugal force, due to the curvature of the path, and (3) the horizontal or gradient pressure, due to gravity. The first two are at right angles to the course of the

FIG. 39.



Deflection and path of winds in frictionless flow under a force of constant magnitude and constant geographic direction.

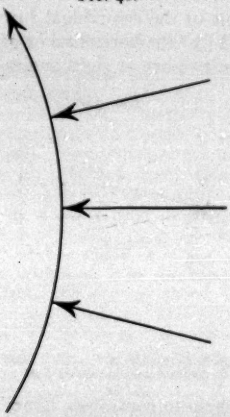
wind and therefore help to control its direction, but do not alter its speed. The latter, however—that is, the gradient pressure—affects both the direction and the speed. Furthermore, as the velocity depends upon the horizontal pressure alone, and as the other forces depend in turn upon the velocity, and are zero when it is zero, it follows that of the three forces only the gradient pressure is independently variable.

Consider, then, the result of applying a horizontal pressure p of constant magnitude and constant geographic direction to a small mass m of air, free, as above assumed, from friction: Let m, Fig. 39, be the mass in question initially at rest with reference

* Continued from page 674, vol. 184, November, 1917.

to the surface of the earth, and let it be acted on by the force p, exactly poleward, say. Immediately the mass moves, under the applied pressure p, the deflective force d becomes operative, thus curving the path (to the right in the northern hemisphere, to the left in the southern) and introducing the centrifugal force c. So long, however, as the angle between the path and the force p is less than 90 degrees there will still be a component of the latter in the line of motion; accordingly the speed of m will continue to increase, and therefore also the deflective force d. If this angle should exceed 90 degrees, the force p would have a component

FIG. 40.



Path of winds in frictionless flow under a converging force.

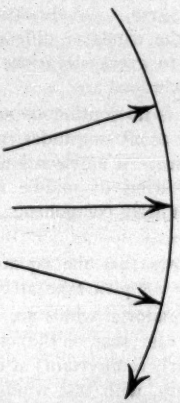
opposite to the direction of motion, which consequently would be slowed up and d thereby correspondingly decreased. In the end, therefore, a poleward force along the meridians on an object free to move gives it an exactly west to east velocity of such magnitude that, except in very high latitudes, the resulting deflective force is nearly equal to the horizontal pressure—the horizontal component of the centrifugal force being then comparatively small, except near the poles. Whatever the direction of the gradient force, whether poleward, as above assumed, or any other, the final motion is normal thereto.

A change in the magnitude but not in the direction of p, above, would only shift the latitude of the path and change the velocity so as to be nearly proportional to p.

If the horizontal pressure is not everywhere in the same direction, but converges, as in Fig. 40, or diverges, as in Fig. 41, the path, in adjusting itself normally to the directions of this pressure, obviously curves, as in cyclonic and anticyclonic regions, respectively.

In all cases, then, the wind automatically follows approxi-

FIG. 41.



Path of winds in frictionless flow under a diverging force.

mately the isobar of its position, with substantially the gradient velocity.

General Relations of Wind to Elevation.—Knowledge of the directions and velocities of the winds of the earth is still fragmentary and incomplete. Over large areas even the surface winds are unknown, and over regions best studied these alone are well known. The continuous records obtained at mountain stations have given much information in regard to air movements, but stations of this nature are comparatively few, and, besides, their data, however valuable, are always affected to an unknown extent by local topography. Cloud observations have also given a large

amount of valuable information, but it, too, is only fragmentary. At best a cloud observation seldom gives more than the direction and velocity of the air at one level, nor does such an observation ever apply to the stratosphere, since this region is never visited by clouds. In many respects kites and sounding balloons have furnished the most valuable data in regard to the movements of the upper air and their causes, but, unfortunately, aerological investigations of this nature, with relatively few exceptions, have been restricted to the northern hemisphere, and even there mainly to the summer season. Nevertheless, by combining the data gathered from these various sources a number of tentative conclusions, subject, of course, to modification, have already been reached in regard to the winds of different parts of the world from the surface up to great elevations. Some of the more important of these conclusions are:

1. That there is no continuous and rapid overflow of the atmosphere at all longitudes from the equatorial to the polar regions. At an elevation of 10 kilometres, for instance, the wind of middle northern latitudes seems to have southerly components about as often as northerly.

From this it follows that the equator-polar circulation is irregular and probably complex even at the higher altitudes.

2. That the equatorial winds are not always and at all levels from the east; that, on the contrary, west winds occur (how regularly is uncertain) at elevations of about 18 to 20 kilometres, with east winds again prevailing (certainly at times) at still greater elevations.

The cause of this layer of equatorial west wind has never been explained. Indeed, it may be only a local and temporary phenomenon.

3. That layers of air in which the temperature increases with increase of elevation, and others in which the temperature is constant, exist at different levels, especially through the first two or three kilometres. This stratified condition of the lower atmosphere appears to be universal. It is found even over tropical oceans, and is exceedingly well developed over the ice plateau of Antarctica.

Each layer usually shows such different humidity and such different wind velocity from those of the adjacent layers as to indicate a distinct origin, which it well may have. As explained, for example, in an earlier section, a rising convection current on reaching its equilibrium level flows away substantially at that particular elevation, and obviously retains its own humidity (provided condensation has not taken place), dust content, and other peculiarities. Its viscosity is not the same as that of the adjacent air, because its humidity or temperature, or both, are different. Hence, as shown by billow clouds, any such layer with a distinctly independent velocity tends to retain its integrity and to glide over another from which it differs physically without rapid intermingling. And there are still other obvious causes of temperature and humidity irregularities and consequent stratification of the atmosphere, such as reflection from, and evaporation of, clouds, surface cooling, and air drainage. Clearly, then, one should expect to find in the lower atmosphere substantially the kind and amount of temperature inversions and other irregularities that it actually shows.

4. That the upper winds are exceedingly variable along the edges of the high-pressure belts, and that marked disturbances occur in the antitrades.

5. That the north-poleward pressure gradient in the upper atmosphere becomes very small long before the arctic circle is reached—in fact, between 50° and 60° N.

6. That in high northern latitudes, where the poleward pressure gradient of the upper atmosphere is small, the westerly winds are not constant.

Local Wind Velocity and Elevation.—Everyone knows that the wind increases with increase of elevation. Even casual observations of such objects as sails of ships, tops of trees, columns of smoke, or isolated clouds suffice to show qualitatively that wind velocity increases with height above the surface; while measurements made by triangulation on freely drifting clouds and balloons, or by anemometry on tethered kites, fully support the conclusions reached by the simpler methods just mentioned. Near the surface of the earth—up to from 2 to 8 metres over an open plain—the condition of the wind, upon whose force this limit depends, may be summarized as follows:

Actual velocity: exceedingly irregular.
Average velocity: increases rapidly with elevation.
Rate of velocity increase: { *a*, increases with average velocity. *b*, decreases with elevation.

Above this thin surface layer the wind increases so nearly regularly with elevation that its approximate velocity at any level up to 16 metres may be computed, according to Stevenson,[38] from its observed velocity at some other height by the empirical equation,

$$V = v\sqrt{\frac{H+72}{h+72}},$$

in which V is the computed wind velocity for the level H in terms of the known velocity v at the height h, both elevations being expressed in feet.

If heights are given in metres, this equation becomes,

$$V = v\sqrt{\frac{H+22}{h+22}}.$$

Other empirical equations expressing the relation of wind velocity to elevation have been given for greater heights. Douglas,[39] for instance, finds that his velocity observations between 100 metres and 600 metres elevation fairly satisfy the simple equation,

$$\frac{V}{v} = \left(\frac{H}{h}\right)^{\frac{1}{4}}.$$

Shaw [40] suggests as a likely formula,

$$V = \frac{H+a}{a} V_o,$$

in which V is the wind velocity at the height H above *ground*, V_o the observed anemometer velocity at a fixed position, and a a constant, obviously depending upon surrounding topography, anemometer exposure, and, perhaps, other factors.

Among the most interesting observations on the relation of wind velocity to altitude are those of Dr. Cesare Fabris,[41] based on some 200 pilot balloon flights made at nearly equal intervals during the year June, 1910, to May, 1911, at Vigna di Valle, the principal aerological station of the Royal Italian Oceanographic Committee. This station is about 25 miles northwest from Rome.

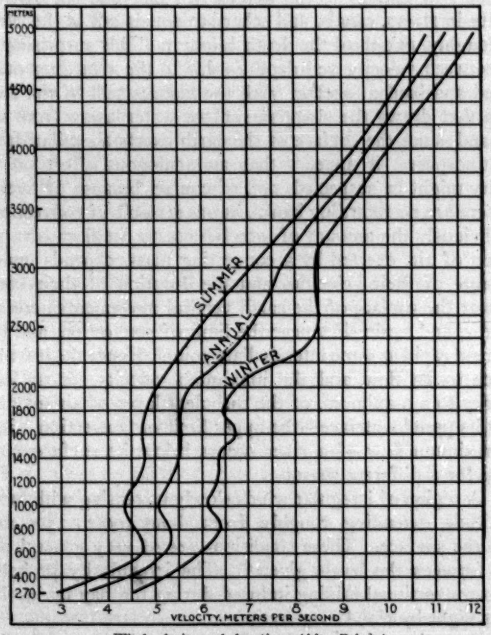
[38] *Jour. Scot. Meteor. Soc.*, 5, p. 348, 1880.
[39] *Nature*, 33, p. 593, 1885.
[40] Advisory Committee for Aeronautics, Reports and Memoranda, 66, No. 9, p. 8, 1909.
[41] *R. Comitato Talassografico Italiano*, Memoria 8, pp. 37–46, 1912.

Its coördinates are: Latitude 42° 04′ 41″ N.; longitude, 12° 12′ 43″ E.; altitude, 272.4 metres.

The general results of all the observations are summed up in Fig. 42, which shows four distinct regions:

a. The region of rapid linear increase of velocity with

FIG. 42.



Wind velocity and elevation. (After Fabris.)

increase of altitude, extending from the surface (272 metres above sea level), where the velocity is least, to an elevation above ground of, roughly, 300 to 500 metres. This obviously is the region in which the winds are affected by surface friction and the resulting turbulence. Clearly, too, the average number of eddies and their consequent effect on velocity must rapidly de-

crease with increase of elevation, at least near the surface, substantially as indicated by the given velocity-altitude curves.

b. The region of velocity decrease with increase of altitude; about 200 metres thick and coming immediately above *a*. This decrease probably is not what one at first would expect, but it may be of fairly general occurrence (conclusive data are not available) in analogy to the well-known fact that the maximum velocity in rivers, canals, and other streams is not at the surface, but, roughly, one-third the depth *below* it. This surprising relation between velocity and depth is due to the retarding drag of the bed and banks, together with the viscous pull of the swifter centre that draws the sluggish surface water away from either side; and, since the surface of the earth exerts a similar drag on the atmosphere, it appears that an analogous effect on wind velocity might be suspected, not, of course, because of overflow, for there are no retarding banks, but as a result of convection.

Obviously the amount of interference to the flow of a given stratum of air, exerted by a convecting mass, depends upon the difference of their velocities and the duration of their contact. But near the surface of the earth vertical movements necessarily are slow, and again slow near the limit of convection, and therefore most rapid at some intermediate point. Hence the least interference to its flow and the maximum velocity, or at least a tendency to a maximum, of the turbulent layer of air may occur below its pseudo surface—the upper limit of convection—just as the maximum flow of a river occurs below its surface, though chiefly for a different reason.

c. A region of irregular winds slowly increasing with increase of altitude, extending, roughly, from about 500 to 1500 metres above the surface. These conditions are of very general occurrence between the levels given.[42] The irregularity probably is due to convectional mixing induced during the day by insolation and at night by cloud evaporation.

d. A region of approximately constant increase of velocity with increase of elevation, beginning at about 1500 metres above the surface and extending to at least the maximum height observed, 5000 metres. The wind velocities of this region, being out of the reach both of frictional and convectional disturbances, are determined by the prevailing horizontal pressure gradients.

[42] Berson, *Wissenschaftliche Luftfahrten*, 3, p. 205, 1900.

Cloud and balloon observations show that increase of wind velocity with increase of altitude beyond 1500 to 2000 metres above the surface holds practically to the top of the troposphere, where the velocity in middle latitudes may amount to as much as 90 metres per second (200 miles per hour) or even more.

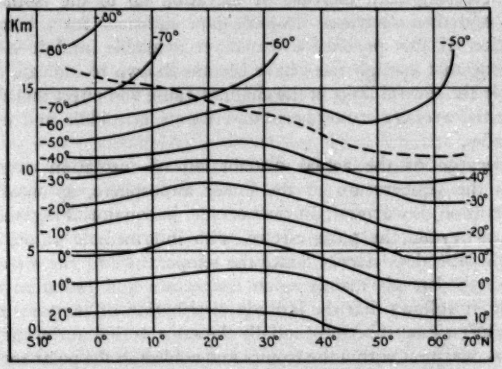
At higher levels—that is, in the stratosphere—the average velocity is decidedly less.

Horizontal Pressure Gradient and Elevation.—All these facts are well known, but there are no generally accepted and satisfactory discussions of the reasons why the average wind velocity at levels above the limit of appreciable surface influence should go on increasing with increase of elevation up to the isothermal level and then decrease. Indeed, data sufficient for a complete solution of this problem are not yet available, and it is only recently that enough facts have become known to indicate at all clearly the several links in the chain of cause and effect that determine the average atmospheric movements in middle and higher latitudes.

Because of the actual distribution of insolation over the earth the temperature of the lower atmosphere, as shown by observation, is warmest, on the average, in equatorial regions and coldest beyond the polar circles, with intermediate values over middle latitudes. Hence, since the temperature of the air above the earth depends mainly upon convection and radiation from below, it follows that the latitude distribution of temperature in the upper air must be substantially the same as that at the surface; that is, warmest within the tropics and coldest in the polar regions, with intermediate values between. And this, indeed, according to kite and balloon records, does apply at each level up to 10 to 12 kilometres, or to fully three-fourths of the air mass. At much higher levels, 15 to 20 kilometres, for reasons that need not be discussed here, the rare atmosphere is coldest over equatorial regions and warmest over high latitudes. This inverse condition, however, does not apply to the winter and summer atmospheres of the same place, nor, presumably, to those of neighboring places on approximately the same latitude. On the contrary, the atmosphere is warmer, on the average, at all explored levels during summer than during winter, and warmer, so far as known, over regions whose temperatures are relatively high than over others of the same latitude that are comparatively cold.

As a crude first approximation to conditions as they actually exist, assume (1) that the temperature distribution is the same along all meridians, (2) that the temperature changes from one latitude to another is the same for all levels, and (3) that sea-level pressure is the same at all latitudes. Assumption (1) approximates the conditions over much the greater portion of the southern hemisphere, but, on account of the irregular distribution of land and sea, has to be modified for any detailed study of the winds of the northern hemisphere. Assumption (2) conforms roughly to average conditions between the thermal equator and

FIG. 43.



Relation of temperature to altitude and latitude. (After Süring.)

latitude 50° to 60°, except near the surface and at altitudes above 10 to 12 kilometres. This is well shown by Fig. 43 referring to the northern hemisphere during its summer, and copied from Süring's paper,[43] on the present state of knowledge concerning the general circulation of the atmosphere. Assumption (3), as applied to normal pressure, is also approximately true except for restricted areas, whose secondary and local effects will not here be discussed.

Consider an atmosphere of the same composition throughout and having initially the same temperature at any

[43] *Zeitschrift der Gesell. für Erdkunde*, p. 600, 1913.

given elevation resting on a horizontal plane. Let the temperature be uniformly increased from north to south, say, and by the same amount from top to bottom, thus simulating the temperature distribution that actually obtains in the earth's atmosphere over middle latitudes, as above explained. Find the resulting horizontal pressure gradient at the different levels.

At the height h the horizontal pressure gradient, $\frac{dp}{dn}$, obviously directed from the warmer toward the colder region, is very approximately given by the equation,

$$-\frac{dp}{dn}=p\frac{\Delta h}{HL},$$

in which L is any given horizontal distance along which dn is taken, p the pressure at the level h, above the colder end of L, Δh the difference of vertical expansion of the air below the level in question at the ends of L, or difference of distance through which the level, whose original pressure was p, was lifted at these two places, and H the virtual height of the atmosphere, approximately 8 kilometres, or height it would have above any point if from there up it had the density which exists at that point. The negative sign is used because the pressure decreases as n, measured from a warmer toward a colder region, increases. For simplicity let L be in the direction of maximum rate of horizontal temperature change, north-south, in this case.

Under the assumed conditions

$$\Delta h=\frac{a}{g}\Delta T h, \text{ approximately,}$$

in which a is the average coefficient of volume expansion of the atmosphere below the level h, and ΔT the difference of temperature change at the ends of L.

At any two levels, then, h and h', the horizontal pressure gradients in the same direction are given approximately by the respective equations,

$$-\frac{dp}{dn}=\frac{p\frac{a}{g}\Delta T h}{HL},$$

and

$$-\frac{dp'}{dn}=\frac{p'\frac{a'}{g}\Delta T' h'}{H'L}.$$

But L may be taken the same in both equations, while a, H, and ΔT generally are not greatly different respectively from a', H' and $\Delta T'$. In reality,

$$\frac{H}{H'}=\frac{T}{T'},$$

and a' is slightly greater than a when T' is less than T. But in this case it appears from observations that actually $\Delta T'$ is slightly less than ΔT, so that

$$\frac{\frac{dp}{dn}}{\frac{dp'}{dn}} = \frac{ph}{p'h'}, \text{ approximately.}$$

Again, from the 5- to the 10-kilometre level, and even to some distance below the former and above the latter,

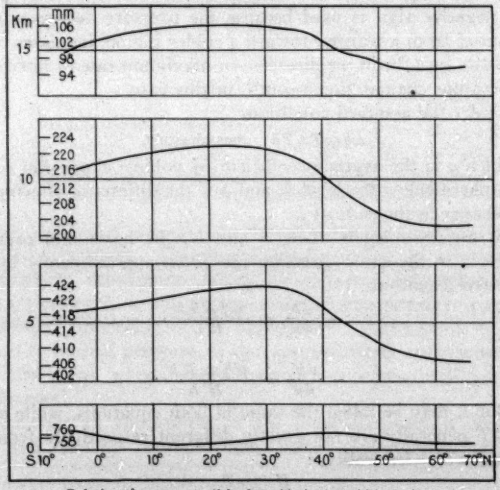
$$\frac{p}{p'} = \frac{h'}{h}, \text{ roughly.}$$

Hence, commonly,

$$\frac{\frac{dp}{dn}}{\frac{dp'}{dn}} = \frac{h'h}{hh'} = 1, \text{ approximately.}$$

That is, through these levels, or from below 5 kilometres to above 10 kilometres, the horizontal pressure gradient established by the temperature difference between adjacent regions of air

FIG. 44.



Relation of pressure to altitude and latitude. (After Süring.)

is roughly constant. This conclusion is fully supported by observations, as shown by Fig. 44, referring to the northern hemisphere during its summer, and also copied from Süring's paper.[44]

Level of Maximum Horizontal Pressure-Gradient.—The approximate level of the maximum horizontal gradient may be found as follows:

As just explained, in the equation,

$$-\frac{dp}{dn} = \frac{p\,\frac{g}{3}\,\Delta T\,h}{HL},$$

the factor, $\frac{\frac{g}{3}\Delta T}{HL}$, is roughly constant. Writing G for the gradient and K for the "constant," the equation takes the form,

$$G = K\,p\,h.$$

Hence G has a maximum value when

$$p\,dh = -h\,dp.$$

But

$$-dp = p\,\frac{dh}{H}.$$

Hence the pressure gradient is steepest when

$$p\,dh = \frac{h}{H}\,p\,dh,$$

that is, when $h = H = 8$ kilometres, roughly.

The following is a slightly different method of arriving at the same conclusion:

The maximum horizontal pressure gradient resulting from a constant temperature difference between two neighboring columns of air obviously is at that level at which the vertical pressure is most changed by the expansion of the air below due to a constant temperature increase.

Let h be any height, and let a be the average coefficient of volume expansion of the air below this level. Then,

$$\Delta h = \tfrac{g}{3}\,h, \text{ nearly,}$$

and

$$\Delta p = \rho\,g\,\Delta h = \rho\,g\,\tfrac{g}{3}\,h, \text{ nearly,}$$

in which ρ is the density of the air at the level h and g the local gravity acceleration.

But $\rho = Cp$, in which C is a constant, and

$$\Delta p = p\,C.g\,\tfrac{g}{3}\,h = K\,p\,h,$$

say, in which K may be regarded as a constant.

[44] *Loc. cit.*

Hence, as before, Δp has its maximum value when

$$p\,dh = -h\,dp = \frac{h}{H}\,p\,dh.$$

That is, the horizontal gradient is steepest when $h = H$. But, as is well known, $H = 8$ kilometres, approximately. Hence the horizontal pressure gradient, resulting from a temperature distribution substantially that which actually obtains in the atmosphere, is greatest at a height of about 8 kilometres.

Constancy of Mass Flow—Egnell's Law.—At a distance above the surface of the earth sufficiently great to avoid appreciable retardation due to friction and turbulence—that is, at elevations greater than 2 kilometres (usually less)—the wind obviously must blow in such direction and with such velocity that there is an approximate equation between the pressure gradient on the one hand and the combined centrifugal force and deflection force due to rotation on the other. Hence, at these levels, if $\frac{dp}{dn}$ is the maximum horizontal pressure gradient,

$$\frac{dp}{dn} = -\rho v\,(2\,\omega \sin\phi + \frac{v}{R}\tan\phi), \text{ approximately.}$$

in which ρ is the density of the air at the level under consideration, v the wind velocity, ω the angular velocity of rotation of the earth, ϕ the latitude, and R the radius of the earth.

A little calculation shows that in the case of a wind following, roughly, a parallel of latitude the second term in the parentheses is always small, except in very high latitudes, in comparison with the first. Thus for a 22.4-metres-per-second (50 miles per hour) west wind at latitude 45° the first is about 30 times greater than the second. Hence, under these conditions,

$$\frac{dp}{dn} = -\rho v\,2\,\omega \sin\phi, \text{ approximately.}$$

But, as just explained, the horizontal pressure gradient, $\frac{dp}{dn}$, is roughly constant between 5 and 10 kilometres elevation and directed polewards. Hence, at any given latitude, ρv, the mass flow, or mass of air crossing unit normal area per unit time, tends to remain constant with change of altitude from 4 or 5 kilometres above sea level up to the isothermal region. In other words, through this region, ρv, at altitude h, equals $\rho' v'$, at altitude h, nearly. This relation between the density and velocity of the atmosphere at different levels is known as Egnell's law,[45] determined empirically by himself, as previously by H. H. Clayton,[46] from cloud observations.

[45] C. R., 136, p. 360, 1903.
[46] *Amer. Met'l Jour.*, 10, p. 177, 1893.

Obviously ρv has a maximum value at that level at which the horizontal pressure gradient is a maximum; that is, at about 8 kilometres above sea level.

Relation of Velocity to Altitude Above 5 Kilometres.—Obviously, if the temperature is constant, as, for simplicity, we may assume it to be,

$$\frac{\rho}{\rho'} = \frac{p}{p'}.$$

But, as already seen, under this condition of constant temperature, through a considerable range of altitude—that is, from below 5 to above 10 kilometres—

$$\frac{p}{p'} = \frac{h'}{h}, \text{ roughly.}$$

Hence,

$$\frac{\rho}{\rho'} = \frac{h'}{h}, \text{ roughly.}$$

But, as explained above, $\rho v = \rho' v'$

Therefore,

$$\frac{v}{v'} = \frac{h}{h'}, \text{ approximately,}$$

or the velocity of the wind through the levels in question is roughly proportional to the altitude.

Above the isothermal level or over the regions between the thermal equator and latitude 50° to 60° the horizontal temperature gradient decreases, and presently even reverses with increase of elevation, as shown by Fig. 43, and therefore the corresponding pressure gradient also decreases, as shown by Fig. 44. Hence, the mass flow, ρv, likewise decreases with elevation above this critical level. Further, the decrease of the horizontal pressure gradient, and consequently of ρv, with altitude in the stratosphere appears usually to be more rapid than that of the density alone, from which it follows that the wind velocity generally must have its maximum value at or below the isothermal level.

Season of Greatest Winds.—From the above discussion it is obvious that the general wind will be swiftest whenever the temperature contrast betwen the air of higher and lower latitudes is greatest. But the temperature of the atmosphere in low latitudes does not change through the year nearly so much as does that of higher latitudes. Hence, the maximum horizontal temperature gradient, and therefore the greatest pressure gradient and strongest winds, must occur during winter.

Latitude of Greatest Winds.—The latitude of strongest winds

clearly is that at which the horizontal pressure gradient is greatest. In the northern hemisphere, according to Fig. 43, this occurs in the summer at about latitude 45°. It is obvious, however, since the pressure gradient depends in general upon the latitude rate of temperature change, that the belt of maximum winds must shift more or less from season to season—poleward with the coming of summer, equatorward with the onset of winter.

Hours of Greatest and Least Winds.—On land, but not appreciably at sea, the velocity of the surface wind has a well-defined daily period. Over comparatively level regions it is least, on the average, about sun-up and greatest from 1 to 2 P.M., with a larger change on clear days than on cloudy. It is also most pronounced in summer, when it reaches an average altitude of about 100 metres, and least in winter, when its depth is only about 40 metres.

The physical explanation of this phenomenon was given long ago by Espy. During the night, when there is no vertical convection, surface friction holds the lower air comparatively quiet, while the upper air glides over the lower with but little restraint. During the day, however, and especially during clear, summer days, vertical convection causes the surface layers of air and those directly above to become thoroughly mixed and therefore to have a more or less common velocity, which, obviously, is greater than the undisturbed or night surface velocity, and less than the undisturbed upper layers before their mixture with the lower.

Daily changes of wind velocity also occur on mountain tops, where the maximum is at night and the minimum by day, or just the reverse of the velocity changes that occur near the surface over plains. Three factors, possibly more, combine to produce this result: (*a*) Contraction of the lower air by night, thus bringing air of slightly higher levels, possibly 15 metres (50 feet) or so, and therefore of somewhat greater velocity down to the mountain top. (*b*) The presence by day and absence by night of surface disturbance, due to convection, in the air flowing over the mountain. (*c*) Overflow from the region of maximum expansion to the region of maximum compression. Since the greatest expansion usually occurs at 3 to 4 P.M. and the greatest compression at 5 to 6 A.M., it follows that the overflow will be from west to east, or with the prevailing winds, through the night, and from east to west, or against them, during most of the day; that is, from sun-up to 3 or 4 P.M.

Daily Direction of the Wind.—The average direction of the wind changes slightly during the day, both over plains and on mountain tops, the tendency being for it always to follow the sun, or, rather, the most heated section of the earth. That is, the wind tends to be east during the forenoon, south (in the northern hemisphere) during the early afternoon, and west during the late afternoon and early evening. This does not mean that at each instant the wind really blows directly from the then warmest region, but that the actual changes through the day in the average hourly wind directions can be accounted for by a velocity component away from that region. The whole sequence results from the thermal expansion of the atmosphere (progressive from east to west), which causes an increase of pressure and consequently an outward flow at all levels above the surface. The area covered is so vast that the time involved, only a few hours, is insufficient for the completion of the convection circuit, so that even the surface winds are *away* from the most heated regions, as stated, and not toward them, as in sea and land breezes, for instance. The compensating or return current occurs at night, when the component, outside the tropics at least, is from the higher latitudes. In reality the entire phenomenon is only a diurnal surge, a flux and reflux, of the atmosphere due to diurnal heating and cooling.

Normal State of the Atmosphere.—From the above explanations of the causes of general winds, especially those that pertain to cloud levels, it appears that the normal state of the atmosphere is one of considerable velocity with reference to the surface of the earth. In middle latitudes, at least, this velocity is from west to east more or less along parallels of latitude and so great as nearly to balance the latitudinal pressure gradient due to the zonal distribution of insolation. Calms, therefore, in this region must be regarded as disturbances of the atmosphere, and indeed often are comparatively shallow, with normal winds above.

Equatorial East to West Winds.—East to west winds are quite as general and constant in equatorial regions as are west to east winds in middle latitudes. Along its borders, roughly 30° N. and 30° S., this equatorial belt of east to west winds is very shallow. Toward the equator its thickness increases, as a rule, until it reaches at least the limit of vertical convection. There are, however, great irregularities in these winds, just as in those of higher

latitudes on either side of it. But the general conditions are as stated and require explanation.

Conceivably the tidal action of the sun and moon on the atmosphere might set it rotating from east to west. But the barometric amplitudes of the atmospheric tides are very small, only about 0.12 m.m. and 0.027 m.m., due respectively to the sun and the moon.[47] Besides, they have but little phase lag, or follow closely under the disturbing body. Hence the tendency of the tide-producing forces to establish an east to west circulation of the atmosphere must be very small.

The diurnal heating and cooling of the air presumably also tends slightly to produce a planetary circulation, possibly in the same direction as that due to the tidal action, or from east to west. In equatorial regions, and in general wherever and whenever days and nights are approximately equal, the atmosphere is most condensed about daybreak, or, say, at 5,30 A.M., and most expanded at about 3.30 P.M. Hence at such times and places the gradient toward the east is to the pressure gradient toward the west substantially as the greatest and least distances, measured along a parallel, between the meridians of highest and lowest temperature; that is, as 7 to 5. On the other hand, the time of flow along the steeper gradient is to the time along the gentler as 5 to 7. But as the distance through which a given mass is moved, provided it is free to move, is proportional to the product of the force acting by the square of the time, it follows that the diurnal temperature changes, neglecting friction, which indeed may even reverse the sense of motion, should give the atmosphere an east to west velocity whose average magnitude would be determined in part by viscosity. The effect of the double diurnal pressure wave on this velocity is uncertain.

However, this thermal effect on wind velocity, whatever its value, clearly is of secondary importance. Possibly it may have some relation to the unexpected east to west winds, the so-called upper trades, reported in the stratosphere over equatorial regions, but many more observations and a more rigid discussion of the theory of atmospheric circulation would be necessary to settle this interesting question.

The only other obvious cause of east to west and west to east general or planetary winds is interzonal circulation, to which,

[47] Lamb, *Proc. Roy. Soc.*, A. 84, p. 556, 1910.

indeed, they usually are regarded as being entirely due. Heating in equatorial and cooling in polar regions necessarily produce a more or less vigorous interchange of air, but, as already explained, one that is profoundly modified by earth rotation.

Assume, as initial conditions, non-rotation, smoothness of surface, uniformity of surface temperature, and absence of local convection. Let the temperature of the surface and the atmosphere now be decreased in proportion to the distance from the equator. There will be a poleward overflow and an equatorward underflow. Further, if, as assumed, there is no local convection—no intermingling of the air at different levels—the equatorward surface air obviously must remain at the surface throughout its course to lower latitudes and then, after rising in the general, not local, convection, move poleward at the top of the atmosphere. Similarly, any other layer must retain, in its equatorial course, a nearly fixed height above the surface and in its poleward journey a corresponding distance below the top.

As a further modification assume again an initial uniformity of surface temperature, but let the earth and the atmosphere be everywhere rotating at the same rate, so that there shall be no winds of any kind. As before, let the temperature be decreased in proportion to the distance from the equator, but let there be no local convection. Again there would be established an upper poleward and an under equatorward circulation, but the air that started toward either polar region would quickly assume an eastward component, while the under- or counter-current would have a westward component. In the absence of friction or other disturbing factor, the upper air moving under a pressure gradient from lower toward higher latitudes would approach along an asymptotic spiral a certain limiting parallel, where the deflecting force due to its final velocity would equal the pressure gradient across that circle. At the same time the east to west under-current would give a deflective force counter to the equatorward gradient. Hence, perhaps, equilibrium would soon be reached with west to east over winds balancing the poleward pressures and east to west under winds balancing the equatorward pressures, and thus further interzonal circulation prevented.

But surface friction, viscosity, local convection, and other disturbing factors so restrict the approach to equilibrium velocities that interzonal circulation is continuous, though of varying

intensity, both local and general. Hence the eastward moving upper air must gradually reach the surface and reach it as an eastward wind. In its subsequent course to lower latitudes it will become a westward wind, as already explained. In general, then, the areas of planetary atmospheric descent are the regions of west to east winds, while the similar areas of ascent are regions of east to west winds. Doubtless, too, these phenomena are accentuated at the surface—that is, the eastward and the westward surface winds are stronger than they otherwise would be—by the intermingling of the air of different levels through innumerable local convections.

What latitude establishes the boundary between the east and west winds? This important question has no answer, not even a theoretical one, unless height is considered. At the surface the boundary is several degrees nearer the equator during winter than in summer, but its average latitude is, roughtly, 30° to 32°. Near its border the east to west winds are very shallow, but in general they increase in depth as the equator is approached until they extend to the limit of vertical convection.

If the temperature distribution were the same along all meridians, and gradually varied from highest at the equator to lowest at the poles, it would seem that the area of ascending air would be substantially the same as the area of descending air (really a trifle larger, because of the higher temperature and consequent greater volume of the ascending air), and therefore that the surface borders between east and west winds would be approximately 30° on either side of the equator. But temperature is not distributed in this ideal way. There are restricted areas which are exceptionally warm, at least during a portion of the year, and others that are exceptionally cold, hence one would expect the area of ascent to be only roughly equal to the area of descent, and therefore the boundaries in question to be, as they are, only approximately at latitudes 30° N. and 30° S.

The velocity of the west to east winds of middle and higher latitudes and the velocities of east to west winds of equatorial regions obviously depend ultimately upon the rate of interzonal circulation. If this circulation were zero, surface friction, facilitated by local vertical convections, soon would greatly diminish and finally eliminate any cross-meridian velocity that originally might obtain. On the other hand, an extremely vigorous inter-

zonal circulation would lead to violent east to west winds, partly because velocity is not altered by mere deflection and partly because there would then be less time for the latitude (conservation of area) effects on the velocity to be minimized by convectional turbulence—the total number of such disturbances becoming larger and their cumulative effects therefore greater with increase of time. Hence the moderate east winds of equatorial regions and west winds of higher latitudes that actually exist are due to the fact that the interzonal circulation itself is moderate—being largely held in check, as already explained, by the automatic formation of gradient winds in the free atmosphere which roughly follow parallels of latitude.

It appears, then, that the temperature gradient, directed in general from the equatorial toward the polar regions, establishes an upper pressure gradient in the same direction and a lower in the opposite direction; that in the absence of friction or other disturbance these pressures would produce east to west and west to east gradient winds with but little or no interzonal circulation; that as the winds actually are more or less checked by surface friction, turbulence, convection, etc., they fail to attain full gradient velocities, and therefore cross the isobars at a small angle, except near the surface, where this angle is much larger, and thus maintain a correspondingly vigorous interzonal circulation even in the absence of cyclones and anticyclones; that the actual west to east winds of the middle and higher latitudes and the east to west winds of equatorial regions are due chiefly to their approach to gradient directions, and, finally, that the strength of any steady wind is proportional, approximately, to the gradient pressure, and its direction substantially normal thereto.

Probable Interzonal Circulation of the Stratosphere.—The primary circulation just explained involves all the atmosphere from the surface of the earth up to at least the highest cloud levels, but there is reason to believe that it does not extend to the greatest altitudes. Indeed, it appears probable that far above the uppermost clouds there may be another primary or fundamental circulation in reverse direction to that of the lower. This inference is based on the fact that the stratosphere is so much warmer in high than in low latitudes that seemingly there must be an overflow of air from the former to the latter and a corresponding return; that is, a primary circulation in the stratosphere in which the upper

branch is from the polar (in this case warmer) toward the equatorial (in this case colder) regions and the under from the equatorial toward the polar regions, with, of course, longitudinal components in each due to the earth's rotation. In a sense the upper circulation, if it exists as inferred, is the mirror image of the lower, though more regular.

In addition to the primary circulation or circulations of the atmosphere as a whole, there are several secondary circulations or wind systems of magnitude sufficient to bring them markedly under the influence of the earth's rotation. It will be convenient next to consider some of the more important of these winds.

CHAPTER IX.

ATMOSPHERIC CIRCULATION (*continued*).

Winds Due to Widespread Heating and Cooling (continued).

MONSOONS.

SUMMER monsoons and winter monsoons, for convenience discussed under the same head, bear the same relation to summer and winter that sea breezes and land breezes bear to day and night. It is the temperature contrast between land and water that establishes the circulation that manifests itself on the surface as a sea or land breeze in the one case and as a seasonal or monsoon wind in the other. The direction of the surface wind in either case is always from the cooler toward the warmer of the adjacent regions, from the ocean toward the land by day as a sea breeze and during the warmer season as a summer monsoon; from the land toward the ocean by night as a land breeze and during the colder season as a winter monsoon. Hence monsoons may be regarded as sea and land breezes of seasonal duration, and might very well be classed with the latter under some common appropriate caption. However, because of the immense areas involved, it cannot be said of them, as of sea and land breezes, that they are caused by mere local temperature differences. Besides, the duration of a land or sea breeze is so brief that it covers only a narrow strip along the coast, as already explained, while the monsoon winds extend far from the coast, both inland and to sea and the directions of the former, since their paths are always short, are but little affected by the rotation of the earth, while the courses of the second are greatly modified by this important factor.

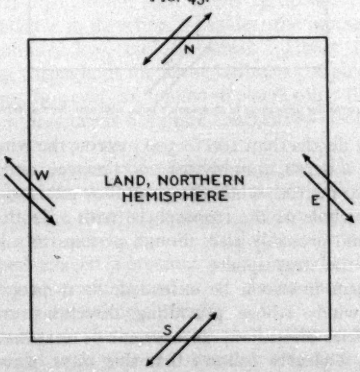
The prevailing directions of monsoon winds, except where distinctly modified by the general circulation, are given by the following table and by Figs. 45 and 46:

Direction of Monsoon Winds

Hemisphere	Season	Land south	Land west	Land north	Land east
Northern	Summer	N. E.	S. E.	S. W.	N. W.
	Winter	S. W.	N. W.	N. E.	S. E.
Southern	Summer	N. W.	N. E.	S. E.	S. W.
	Winter	S. E.	S. W.	N. W.	N. E.

Since monsoons depend upon seasonal temperature contrasts between land and water, it is obvious that winds of this class must be most pronounced where such contrasts are greatest—that is, in temperate regions—and least developed where the temperature contrasts are smallest—that is, in equatorial and polar regions. It is even possible for secondary monsoons to develop, or for a monsoon to occur within a monsoon. This merely requires a

FIG. 45.

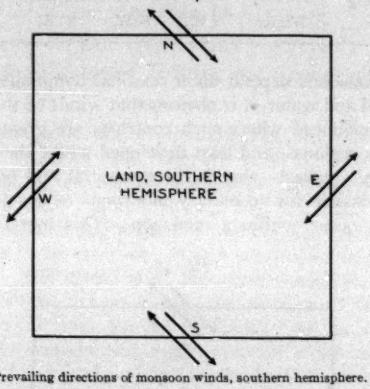


Prevailing directions of monsoon winds, northern hemisphere.

favorably situated inland sea, such as the Caspian. In such cases monsoons or seasonal winds prevail between the inland sea and the surrounding land, and in turn between the continent as a whole and the adjacent oceans, just as, and for the same reason that on a still greater scale, there is a constant circulation between the perpetually warm equatorial regions and those about the poles that are continually cold.

Another comparison between these several winds, the semi-daily (land and sea breeze), semi-annual (monsoon), and perpetual (interzonal), that is interesting and instructive concerns their depth. As already stated, the land and sea breezes seldom

FIG. 46.



Prevailing directions of monsoon winds, southern hemisphere.

reach greater depths than 100 to 500 metres; the winter monsoon of India has a depth, roughly, of 2000 metres, and the summer monsoon 5000 metres; while the general or interzonal circulation involves the whole of the troposphere with a depth of 10 to 12 kilometres, and probably also, though perhaps to a less vigorous degree, even the stratosphere.

If the term monsoon be extended, as it properly may, to include all winds whose prevailing directions and velocities undergo distinct alterations as a result of seasonal changes in temperature, it clearly follows that this class of winds is well nigh universal. Nevertheless, it is generally thought of in con-

nection with only those places where it is most strongly developed, and especially where the seasonal winds are more or less oppositely directed. Among these places are: India (Indian monsoons are the most pronounced of all and have been most fully studied), China, the Caspian Sea, Australia, and portions of Africa.

In the United States the chief monsoon effects are in the eastern portion, where the prevailing winds are northwest in winter and southwest in summer, and in Texas, where the prevailing winds are also northwest in winter but southeast in summer.

TRADE WINDS.

As previously stated, in equatorial ocean regions, or, roughly, over the oceans between latitudes 30° N. and 30° S., the winds usually have an east-to-west component. In the northern hemisphere they blow rather constantly from the northeast, becoming east-northeast and finally nearly east winds as the equator is approached. Similarly, in the southern hemisphere, starting from the southeast, they gradually back through east-southeast to nearly east. In each case they blow "trade"; that is, in a fixed or nearly fixed direction. It is because of this steadiness of direction and not because of any relation they may have to the paths of commerce that they are called trade winds. Along each border of this belt, or along both the northern and southern horse latitudes, calms are frequent, while such winds as do occur generally are light and variable in direction. Besides, the barometric pressure is high, humidity low, and sky clear. Hence it generally is inferred that throughout the horse latitudes the air is descending. This evidence, however, as applied to places other than the centres of maximum pressure is not quite conclusive—it only shows that the air is not ascending.

Another narrow belt of calms or light variable winds, known as the region of the doldrums, approximately follows the equator (more exactly the thermal equator), where the two systems of trade winds, the northern and the southern, come together. Here, however, the barometric pressure is low, humidity high, and skies often filled with cumulus and other clouds that give conclusive proof of strong ascending currents.

Trade winds in the sense here used—that is nearly constant winds blowing in a westerly direction—do not occur on land except along coasts and over islands. Besides being well-nigh

peculiar to the oceans, they are even different from ocean to ocean, and also, since they tend to follow the thermal equator, somewhat different in latitude and intensity from season to season.

According to Shaw the average velocities of the Atlantic trade winds are as follows:

Trade-wind Velocities, Atlantic Ocean.

	Jan.	Feb.	Mar.	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Year	
N. E. trade...	11.9	13.0	13.5	13.4	12.3	11.4	10.3	8.3	9.6	7.4	9.8	11.6	10.5	miles hour
N. E. trade...	14.1	13.0	13.0	12.1	11.0	12.1	12.1	15.0	17.0	15.0	16.1	15.0	13.9	miles hour

From this it appears that the trades are strongest during the winter when their counterpart, the system of westerly winds of higher latitudes, is strongest; and weakest during the summer when their counterpart is weakest. It also appears that the south-trades, or those pertaining to the southern hemisphere, are about one-third stronger than the northeast trades, due probably to the greater extent of the southern oceans and consequent less surface friction—the same reason, doubtless, that the westerly winds of the southern hemisphere are stronger, on the average, than the westerlies of the northern hemisphere.

The trade winds of the Pacific Ocean are weaker than those of the Atlantic and not so constant in direction. On the Indian Ocean the trades are confined to the southern hemisphere. North of the equator the winds of this ocean, being controlled by the adjacent continent, are distinctly of the monsoon type.

The seasonal shifting in latitude of the trade regions and belt of doldrums is shown by the following table, copied from Hann's Lehrbuch, 3d edition, p. 463:

Seasonal Latitude Limits of Trade Winds and Doldrums.

	March		September	
	Atlantic	Pacific	Atlantic	Pacific
N. E. trade.	26°–3°N	25°–5°N.	25°–11°N.	30°–10°N.
Doldrums...	3°N.–Equator	5°–3°N.	11°– 3°N.	10°– 7°N.
S. E. trade..	Equator–26°S.	3°N.–28°S.	3°N.–25°S.	7°N.–20°S.

ANTITRADE WINDS.

As the heated and expanded air of equatorial regions overflows to higher latitudes it necessarily is deflected by the rotation of the earth. That portion which goes north changes from an east wind

near the equator to a southeast, south, southwest, and, finally, at about latitude 35° N., a more nearly west wind. Similarly, that portion which goes south becomes northeast, north, northwest, and, finally, at about latitude 30° S. a more nearly west wind.

At great altitudes, 10 to 15 kilometres, the east-to-west velocity near the equator is, roughly, 36 metres per second (80 miles per hour). Hence its west-to-east velocity around the axis of the earth is about 428 metres per second (957 miles per hour). As this air, assuming it to start from the equator and neglecting viscosity effects, moves to higher latitudes its west-to-east velocity must so increase, according to the law of the conservation of areas, that at about 16° N. or S. its angular velocity will be the same as that of the earth, and itself, therefore, be moving only poleward in the plane of the meridian. The exact latitude, however, at which the antitrades move directly poleward depends upon the position of the thermal equator and therefore varies with the seasons. Thus during August and September, when the centre of the doldrums is, roughly, 8° N., the inflection of the northern antitrades occurs somewhere between latitudes 20° N. and 25° N. At other seasons, because the doldrums are then nearer the equator, the place of inflection is also less removed. Beyond the turning point, wherever that may be, these upper or antitrade winds become westerly, and, except as modified by local disturbances, tend, as previously explained, to reach, under the influence of the poleward pressure, a limiting or gradient velocity and to follow parallels of latitude. However, there are innumerable disturbances, mainly due to the distribution of land and water, that cause constant and abundant interzonal circulation which feeds and indefinitely maintains the antitrade wind portion of the general or planetary atmospheric circulation.

The height of the antitrades (depth of the trades) is greatest, at any given place, during summer and least during winter. It also decreases with latitude, becoming zero, on the average, at about 30° N. and S. Thus during winter their height over Cuba, 22° N., is about 3.5 kilometres; over Jamaica, 17° N., 6.5 kilometres; over Trinidad, 12° N., 8 kilometres, and over Hawaii, 19° 30′ N., about 3 kilometres. But whatever their height it is always the same as the depth of the trades of which they are but the overhead continuation. Indeed, the trade winds as they ap-

proach the equator ascend and gradually flow off poleward, thus producing in each hemisphere a great antitrade branch of the general circulation, which in turn becomes the westerlies of higher latitudes. These, in their turn, are confused by storms and other local disturbances, but after few or many vicissitudes, as circumstances may determine, ultimately return to a similar starting-point, only to begin another of their endless cyclic journeys through trades, antitrades, westerlies, and the innumerable secondary winds such a course implies.

TROPICAL CYCLONES.

A tropical cyclone—the cyclone of the Indian Seas, the hurricane of the West Indies and South Pacific, and the typhoon of the West Pacific and China Sea—consists of a vast whirl of rapidly moving air currents surrounding a calm and relatively small centre or vortex.

Distinction Between Tropical and Extra-tropical Cyclones.—Although tropical and extra-tropical cyclones have many similarities, such as low-pressure centres, abundant precipitation, same instantaneous wind directions, and the like, and although it may be impossible to say just when a tropical cyclone on its way to higher latitudes becomes extratropical in character, nevertheless they usually differ from each other in several important respects. Among these differences are: (*a*) The isobars of the tropical cyclone generally are more symmetrical and more nearly circular than those of the extra-tropical. (*b*) The temperature distribution around the vortex of the tropical cyclone is practically the same in every direction, while about the extra-tropical it is very different. (*c*) In tropical cyclones rains are torrential and more or less equally distributed on all sides of the centre; in the extra-tropical rains usually are much lighter and very unequal in different quadrants. (*d*) Tropical cyclones usually have calm rainless centres 10 to 50 kilometres (6 to 31 miles) or more in diameter, while the extra-tropical rarely show this characteristic whirl phenomenon. (*e*) Tropical cyclones are most frequent during summer of the hemisphere in which they occur, while the extra-tropical are strongest and most numerous during winter. (*f*) Tropical cyclones often move to higher latitudes, where they assume, more or less completely, characteristics of the extra-tropical; the extra-tropical, on the other hand, never invade the

region of the tropical nor assume its distinctive characteristics. (*g*) The pressure-drop of the tropical cyclone generally begins with the winds; in the extra-tropical it usually begins much sooner. (*h*) The tropical cyclone has no anticyclone companion; the extra-tropical usually has—to the west.

Place of Occurrence.—Tropical cyclones occur over the warmer portions of all oceans except, possibly, the South Atlantic. They are most numerous, however, in the west Atlantic (including the Gulf of Mexico), Bay or Sea of Bengal, and west Pacific (including the China Sea), where their annual frequencies are, roughly, about 4, 8 and 24 respectively. They seldom originate closer than 5° or 6° to the equator but most frequently between latitudes 10° and 20.° In fact, they seem to originate almost entirely along the belt of doldrums, and therefore, since this belt follows the sun, to appear at higher latitudes during summer and lower, or not at all, during winter.

Size and Shape of Storm.—The diameter of the tropical cyclone varies greatly. Near their origin some may be no more than 80 kilometres (50 miles) across, while others, when well developed, may have diameters of 300 to 1500 kilometres (187 to 932 miles). The clouded area incident to typhoons, always much more extensive than the surface storm, may be even 3000 kilometres (1864 miles) across.

The shape of the storm, as given by the isobars, appears usually to be that of an ellipse whose diameters are to each other, roughly, as 2 to 3, with the longer axis in the direction of travel.

Direction of Wind.—The surface direction of the wind is spirally in at an angle of 30 degrees, roughly, to the isobars, counter-clockwise in the northern hemisphere, clockwise in the southern. At an elevation of only 700 to 800 metres the inflow is said to cease, and above this level the circulation is outward. These horizontal motions necessitate a correspondingly strong upward component around the vortex or inner portion of the storm, and a slower downward component over a much greater surrounding area.

Velocity of Wind.—The velocity of the wind in a tropical cyclone also varies greatly from one storm to another, and even more from one to another portion of the same storm. Near the centre, or within the eye of the storm, which may have any diameter from 8 to 50 kilometres (5 to 31 miles) or more, the

wind is very light and the sky clear or only partially covered with high clouds. Away from this centre, especially on the poleward side, the winds often reach destructive velocities of 40 to 50 and even 60 metres per second (90 to 112 or even 134 miles per hour), but decrease in violence rather rapidly with increase of distance from the centre; dropping to only moderate winds of 50 to 60 kilometres (31 to 37 miles) per hour at a distance of, say, 300 kilometres (187 miles).

Direction of Travel.—Tropical cyclones of the northern hemisphere first move west, then usually northwest. Many turn north at latitude 20° to 25°, roughly, and finally move away to the northeast. In the southern hemisphere the corresponding directions of travel of the tropical cyclone are: West, southwest, south, and, finally, southeast.

Velocity of Travel.—The velocity with which tropical cyclones travel varies from almost zero in certain cases, especially at or near the place of inflection when this happens to be abrupt, to perhaps 800 kilometres (497 miles) per day. Over the Bay of Bengal, Arabian Sea, and China Sea the velocity averages about 320 kilometres (199 miles) per day. Over the south Indian Ocean the velocity ranges from 80 to 320 kilometres (50 to 199 miles) per day. Over the west Atlantic the average velocity before and during recurvature is about 420 kilometres (260 miles) per day, but after recurvature—that is, when moving northeast over middle latitudes—about 640 kilometres (398 miles) per day.

Origin and Maintenance.—Since tropical cyclones originate in a belt or region of doldrums where convectional rains are frequent and heavy, and since they rarely occur closer than 5° or 6° of the equator, it follows that both vertical convection and earth rotation are essential to their genesis.

The atmosphere of a doldrum belt becomes very warm and humid, and therefore frequently is in a state of vertical convection. The upward branches of this convection are nearly always limited to very restricted areas, where they break through, as it were, and often give rise to local thunderstorms. Occasionally, however, heating and expansion must take place more or less uniformly over a comparatively extended region. So long as the upward current is gentle and restricted to a small area, the compensating inflow from the sides is also gentle and can produce

only a cumulus cloud and perhaps a thunderstorm. In the event that such a storm is formed, the inflowing counter-current to the ascending warm air is replaced by an equivalent column or sheet of descending cold air immediately to the rear. That is, the loss of warm surface air is compensated by a similarly concentrated and vigorous downflow of cold upper air. Hence, rotary circulation since it depends upon horizontal inflow from all, or at least several, sides, is not possible in the case of ordinary thunderstorms, whatever their location.

On the other hand, an approximately equal expansion of air over a relatively large area, whether caused by an increase of temperature, or vapor density, or by both, must lead to an overflow above and a corresponding surface inflow around the outer borders.

Obviously the rate of volume overflow at any time is proportional to the area in question, while the corresponding inflow is proportional to the boundary multiplied by the average normal component of the wind. If the area is circular with radius R, it follows that the rate of outflow above is proportional to πR^2, and the rate of inflow below to $2\pi RV_n$, in which V_n is the average radially inward component of the wind at the distance R from the centre. But as the two currents compensate each other except as modified by precipitation, explained below, it follows that V_n, other things being equal, is proportional to R. Hence, when the area involved is rather large, 100 miles, say, in diameter, the relatively shallow and spirally moving compensating or return current may become very perceptible. This at once feeds the entire rising column with excessively humid air that renders it an even better absorber than before of both insolation and terrestrial radiation and increases its rate of expansion, thus initiating, perhaps, a widespread condensation. If so, the latent heat thus set free, while it does not actually raise the temperature of the air, reduces the rate of adiabetic cooling from approximately 1° C. to about 0.4° per 100 metres increase of elevation, and thereby establishes within the rising column temperatures distinctly higher than those of the surrounding air at the same level. In this way the circulation is accelerated, and thereby the rate of condensation and freeing of latent heat increased until, through growth of size, restricted supply of water vapor, and other causes, a limiting, somewhat steady, state is attained.

When the conditions here described occur at some distance from the equator the rotation of the earth deflects the inflowing air and establishes a rotation around the region of lowest pressure —an effect all the more likely to occur, and to an accentuated extent, when the existing convection takes place along the doldrum boundary between the rather oppositely directed (not opposing) trade winds, the one from higher latitudes, the other from across the equator. But whatever the radius of curvature, the angular momentum remains constant—the law of the conservation of areas obtains—except as modified by friction and viscosity, and therefore, since surface-drag is effective at but small elevations, the atmosphere at only 100 to 200 metres above the water may, as it moves inward, soon reach that velocity at which its deflective force is equal to the horizontal pressure gradient. When such velocity is reached, as it obviously may be at any appreciable altitude, inflow at that place necessarily ceases. Near the water, however, this limiting velocity is prevented by surface friction. Hence, as soon as the whirl is well established, it must be fed almost exclusively by the lowest and therefore most humid air. In this way a maximum amount of precipitation, and, through it, a maximum amount of thermal energy, is secured—a condition important to the maintenance of the tropical cyclone, as is evident from the fact that it tends to go to pieces over dry land, especially before it has recurved and become essentially extra-tropical.

Of course, similar atmospheric expansions may, and doubtless do, occur in the doldrums when they are on or very close to the equator, but in this case a whirl is impossible, and therefore a low so initiated will soon fill by gentle, somewhat radial, winds from all sides and at considerable altitudes, or, at most, mere local thunderstorms will develop.

From the above it is evident that the seat, so to speak, of the tropical cyclone is where the sustaining energy is supplied; that is, where condensation is taking place. Hence the movement of the air at this level, and not at the surface, determines the course of the storm, and even carries it athwart shallow surface winds.

(To be continued.)

THE VERTICAL DISTRIBUTION OF DISSOLVED OXYGEN AND THE PRECIPITATION BY SALT WATER IN CERTAIN TIDAL AREAS.*

BY

J. W. SALE AND W. W. SKINNER.

BIRGE and Juday [1] have shown that dissolved oxygen is deficient in the lower layers of water of 129 inland lakes of Wisconsin, due to thermal stratification of the water and subsequent depletion of the oxygen in the colder layers by the process of respiration of plants and animals, by the direct oxidation of dead organic matter, and by the decomposition which results from the action of bacteria.

Data obtained by the Water Laboratory of this Bureau show that less dissolved oxygen is present in the water near the bottom of the Potomac Estuary and of portions of the Chesapeake Bay than in the surface water, apparently due to the under-run of salt water present in those waters and the subsequent depletion of the oxygen in the lower layers as indicated by Birge and Juday.

Other data obtained show that maximum turbidity of two tidal rivers is attained in the regions where salt water first appears.

The two phenomena of depleted dissolved oxygen content and of maximum turbidity at the junction of fresh and salt water are related in that the sedimentation caused by the salt water is a contributing factor in the depletion of the oxygen of the lower layers of water.

These data are of particular interest at this time because of the possible relation which the dissolved oxygen content bears to the mortality of fish and shellfish, reported as occurring at the mouth of the Potomac and of other rivers flowing into Chesapeake Bay and in other tidal waters. It is thought that the dissolved oxygen content of those waters may have a profound influence on fish life, particularly on the migration of fish in those regions.

Helland-Hansen [2] noted a deficiency of oxygen in the lower

* Contribution from the Water Laboratory, Bureau of Chemistry, U. S. Department of Agriculture. Communicated by Doctor Skinner.

water of some oyster ponds situated in Norwegian fjords. These ponds were connected with the main bodies of water in the fjords only during unusually high tides. The deficiency of dissolved oxygen threatened the destruction of the oysters.

The content of chlorin, turbidity, and dissolved oxygen of about 275 surface and deep samples collected from the lower Potomac River, Maryland, the Maurice River, New Jersey, the

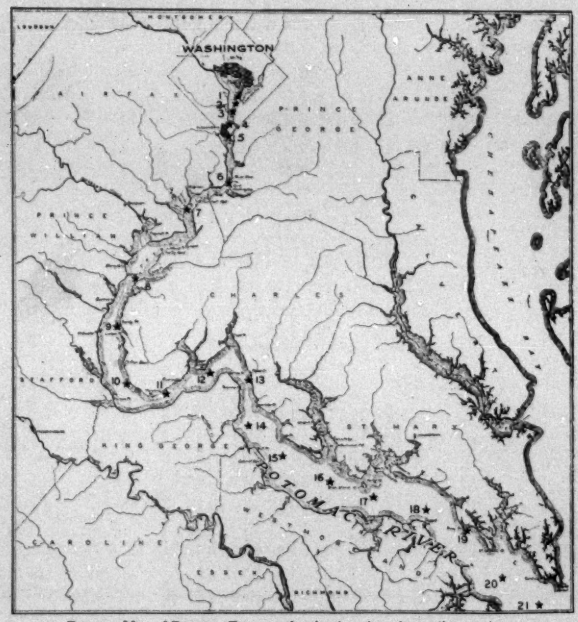


FIG. 1.—Map of Potomac Estuary, showing location of sampling stations.

Approximate depth in feet at Sampling Stations in lower Potomac River:

No. 1, 27;	No. 2, 33;	No. 3, 27;	No. 4, 31;	No. 5, 33;
No. 6, 20;	No. 7, 34;	No. 8, 33;	No. 9, 30;	No. 10, 27;
No. 11, 24;	No. 12, 45;	No. 13, 32;	No. 14, 34;	No. 15, 27;
No. 16, 43;	No. 17, 27;	No. 18, 30;	No. 19, 75;	No. 20, 75;
No. 21, 75.				

Chesapeake and the Delaware Bays have been plotted for purposes of comparison, the mutual relations being shown clearly in the accompanying curves. Seasonal temperature and chlorin curves for the lower Potomac River are contained in Figs. 8

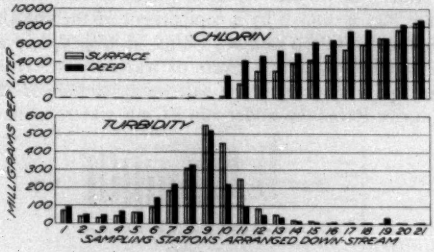


FIG. 2.—Lower Potomac River, Washington, D. C., to Point Lookout, March 11–13, 1912.

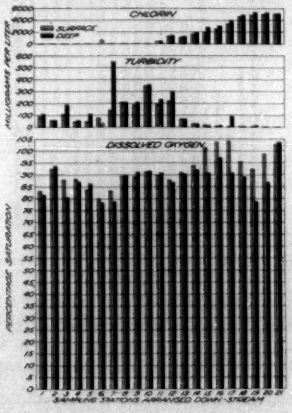


FIG. 3.—Lower Potomac River, Washington, D. C., to Point Lookout, April 29–May 9, 1912.

and 9. All curves have been arranged to extend down stream or down the bay. The locations of the sampling stations in the lower Potomac River are shown on the map, Fig. 1. The so-called surface samples were collected about one foot below the

surface and the deep samples about three feet from the bottom. The methods of examination used were those recommended by the A. O. A. C., published in the *Journal of the A. O. A. C.*, vol. 2, No. 4.

The under-run of salt water in the Potomac Estuary and Chesapeake Bay is shown by a comparison of the chlorin curves for the surface and deep samples (Figs. 2, 3, 4, 5, 6, 7 and 10). It will be noted that the two layers of water of different specific gravity are quite distinct in the salt-water section of the river. In the Maurice River the under-run of salt water, while present,

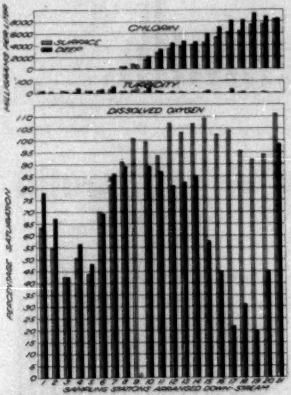


FIG. 4.—Lower Potomac River, Washington, D. C., to Point Lookout, September 21, 22, 1912.

is not so noticeable, the mixing of the water in that locality being fairly complete when samples were collected in November, 1912 (see chlorin curves, Fig. 11).

A comparison of the turbidity curves with the chlorin curves for both the Potomac and Maurice Rivers shows that, with two exceptions, which are evidently abnormal (Figs. 3 and 5), maximum turbidity is attained at the station where the content of chlorin begins to increase (Figs. 2, 4, 6, 7, 11). This relation is most evident when the fresh water of the rivers is quite turbid (Figs. 2, 3, 7), and indicates a precipitation of matter which had been dissolved in the fresh river water. A noticeable feature of

the turbidity curves is that the rise to a maximum and the fall take place within a few sampling stations above and below the rise in salinity.

Cummings [3] has stated that the area from Indian Head to Maryland Point in the lower Potomac River is a great natural basin in which sedimentation is caused by the irregularity in velocity and direction of current and by the admixture of enormous volumes of sea-water, with its inability to carry large proportions of suspended matter.

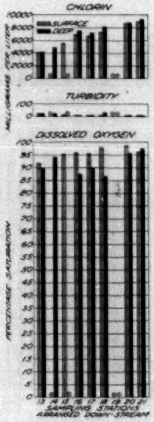


FIG. 5.—Lower Potomac River, off Pope's Creek, Maryland, to Point Lookout, October 24, 25, 1912.

These conclusions are confirmed by the data expressed in graphic form in Figs. 2, 3, 4, 6, 7.

An inspection of Chart No. 559 of the United States Coast and Geodetic Survey for the section of the lower Potomac River extending from lower Cedar Point to Mattawoman Creek shows an extensive series of flats between Maryland and Sandy Points, which it is believed have been formed by the precipitating and coalescing action of the salt water and subsequent sedimentation of the suspended matter. The channel of the river for a considerable distance opposite these flats is very narrow. For in-

stance, off Douglass Point the river is about 2.7 miles wide, while the channel of the river is only about one-tenth of this distance, or 0.27 mile.

A study of the relations of the dissolved oxygen curves to the chlorin curves shows that when an under-run of salt water is present the dissolved oxygen curves for the deep samples are considerably lower than the curves for the surface samples, showing less dissolved oxygen in the deep samples than in the surface samples. When an under-run of salt water is absent (that is, when the water is practically uniform in composition),

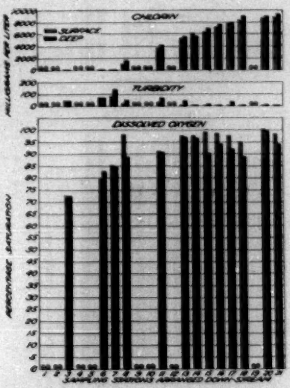


FIG. 6.—Lower Potomac River, vicinity of sewage outlet, to Point Lookout, December 3, 4, 1912.

the dissolved oxygen curves are closer together, or the deep samples may contain even more dissolved oxygen than the surface samples. For example, in September, 1912 (Fig. 4), the curves for surface and deep samples are relatively close together in that area of the lower Potomac River extending from Stations 1 to 7, while from Stations 8 to 21 they are widely separated. The chlorin curves show that above Station 7 the water was uniform in composition, while below Station 7 there was a marked under-run of salt water.

It is probable that the under-run of salt water in the Potomac Estuary and in Chesapeake Bay interferes with the distribution

of oxygen by reason of its greater specific gravity, which keeps the denser water persistently on the bottom, thus hindering the mechanical mixing of the water by tides, winds, etc.

This stratification, due to concentration, is very persistent in the Potomac Estuary. It was present without exception each time samples were collected from that area under widely varying conditions of the weather. For example, on October 24, 1912, the wind was very high and the water of the estuary was very rough. For several days prior to this date a strong northwest wind had lowered the level of the water appreciably. Nevertheless, this

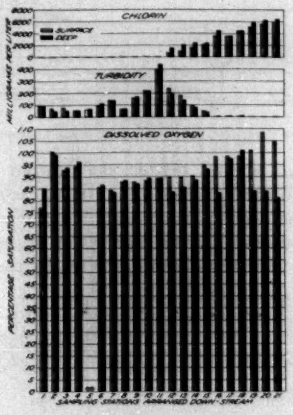


FIG. 7.—Lower Potomac River, Washington, D. C., to Point Lookout, April 15-17, 1913.

extreme agitation of the water of the estuary did not effect a uniform mixing (Fig. 5). Also, a few days prior to April 15, 1913, heavy rains occurred, following a rather dry season of about a month. The flood at this time pushed back the incoming salt water to Station 11, between Maryland Point and Riverside, some thirty miles below Station 7, off Whitestone Point, which was the upper limit of the salt water in September and December, 1912 (Figs. 4, 6, and 7). It will be noted that the under-run of salt water, together with the depleted oxygen content in the lower layer of water, persisted under these conditions.

The dissolved oxygen content has been expressed in percentage saturation. The lower curves for dissolved oxygen in the deep samples, therefore, represent an actual consumption of oxygen.

Since dissolved oxygen is consumed chiefly by the decomposi-

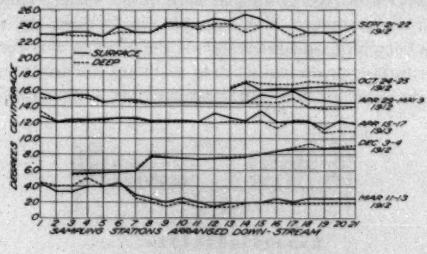


FIG. 8.—Lower Potomac River, Washington, D. C., to Point Lookout. Seasonal variations in temperature.

tion of inanimate organic matter, the stratum of water nearest to the decaying organic matter would suffer the greatest depletion of oxygen. The decomposable organic matter may be obtained from several sources. During high water in the river, a portion of the material which has been deposited by the process of salt-

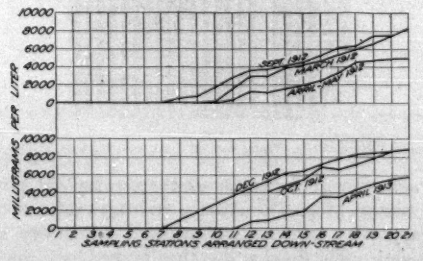


FIG. 9.—Potomac River chlorin curves, March, April, September, October, December, 1912, and April, 1913. (Surface samples.)

water precipitation referred to above, and by sedimentation in a rather restricted area, is stirred up and swept down stream with the current, to again gradually settle out over a larger area of bottom or to be collected in other portions of the river, favored because of the contour of the bottom or by the currents. Another

source of decomposable matter is plankton forms, which die, settle to the bottom, and decompose. Purdy [4] has shown that the volume of plankton in the Potomac River in the vicinity of Point Lookout is greater than in any other portion of the lower river.

Broken-down, submerged plants, leaves, elutriated soil, and other débris which are carried into the estuary and bay by

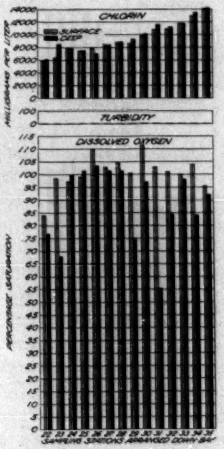


FIG. 10.—Chesapeake Bay, Annapolis to Portress Monroe, September 20 and October 3, 1912.

Sampling Station, No.	Date collected	Depth, feet	Location
22	10–3–12	50	Off Annapolis.
23	10–3–12	50	One mile south Kent Island Light.
24	10–3–12	50	Off mouth Great Choptank River.
25	10–3–12	40	About two miles above Cove Point.
26	10–3–12	30	Off mouth Patuxent River.
27	10–3–12	30	Just above Point No Point Light.
28	10–3–12	24	Off Point Lookout.
29	9–20–12	60	4¼ miles off Smith Point Light.
30	9–20–12	30	9 miles off mouth Great Wicomico River.
31	9–20–12	40	10 miles off mouth Rappahannock River.
32	9–20–12	35	6 miles off shore, south of Piankatank River.
33	9–20–12	35	4 miles off Mobjack Bay.
34	9–20–12	30	13 miles off mouth of York River.
35	9–20–12	30	8 miles off Buckroe Beach.

numerous tributaries also furnish their quota of decomposable matter.

A certain amount of dissolved oxygen is consumed in the life-processes of marine organisms.

The dissolved oxygen, therefore, in the dense bottom layer of water is depleted chiefly by the decomposition of dead vegetable

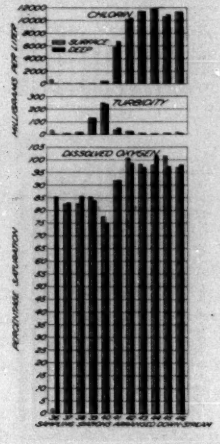


FIG. 11.—Maurice River and Delaware Bay, Millville to Egg Island Light, November 19, 20, 1912.

Sampling Station, No.	Date collected	Depth, feet	Location
36	11–19–12	12	Maurice River, at Millville.
37	11–19–12	12	Maurice River, at Kees Landing.
38	11–19–12	24	Maurice River, off Buckshuten.
39	11–19–12	26	Maurice River, at Morristown Bridge.
40	11–19–12	33	Maurice River, ¼ mile below Menhaden.
41	11–19–12	14	Maurice River, at mouth.
42	11–20–12	11	Delaware Bay, 5 miles S. by E. of East Point Light.
43	11–20–12	12	Delaware Bay, 5 miles S. of East Point Light.
44	11–20–12	13	Delaware Bay, 1½ miles S. W. Egg Island Light.
45	11–20–12	18	Delaware Bay, just outside False Egg Island.
46	11–20–12	9	Delaware Bay, about ⅓ mile off Egg Island Light.

and animal matter gathered from various sources, while the stratification of the water due to difference in specific gravity prevents a restoration of the supply from the saturated or supersaturated upper layers of water by hindering the mechanical mixing of the water by the tides, winds, etc.

The maximum reduction of dissolved oxygen in the Potomac Estuary and Chesapeake Bay was found in September and represents late summer conditions. At Stations 15 to 20 on this trip the dissolved oxygen was reduced to 57.5, 45.1, 21.6, 30.8, 19.7, and 45.1 percentage saturation. The actual volumes of oxygen (0° C. and 760 mm.), corresponding to the above figures for percentage saturation, are 3.2 c.c., 2.5 c.c., 1.2 c.c., 1.7 c.c., 1.1 c.c., 2.5 c.c., respectively (see Fig. 4).

It is to be expected that the maximum reduction in the dissolved oxygen content of the denser bottom layer of water would occur at this season of the year, since the supply of decomposable organic matter from plankton form, vegetation, etc., is greater during the summer months, and bacteria which assist in the breaking down of the organic matter are most active at this season, because of the higher temperature. It will be noted, from an inspection of the curves for seasonal variation in temperature (Fig. 8), that the water was about 23° C. at this time. In October the temperature had fallen to about 17° C., and in March was about 2° C., the lowest temperature noted.

Lebedinzeff [5] reported diminished dissolved oxygen content at depths of 183 to 200 metres in the Black Sea, and it is of interest to note that no life was found below 183 metres. As in the Potomac Estuary and Chesapeake Bay, vertical circulation was cut off in the Black Sea by stratification due to increase in concentration with increased depth.

It appears that thermal stratification may exist to a slight extent in the Potomac Estuary (Fig. 8). However, the variation in temperature of the surface and deep samples is generally of the order of 1° C. or less. This body of water may be regarded, therefore, as homothermous.

The chlorin and dissolved oxygen curves for May, 1912, and for April, 1913, are very similar, and their comparison is of interest, as showing the annual recurrence of seasonal conditions (Figs. 3 and 7).

SUMMARY.

It has been shown that the lower layers of certain tidal waters under investigation contain less dissolved oxygen than the upper layers. Evidence has been presented to show that this phenomenon is caused by the stratification of the water due to the specific gravity of the under-run of sea-water, which cuts off vertical circulation, and to the subsequent depletion of the oxygen in the lower layers by natural agencies. The depletion of oxygen was found to be greatest in September. The precipitation and sedimentation of matter in tidal areas by sea-water have been presented in graphic form. These data are considered to be of particular interest from the viewpoint of fish and shellfish life.

WASHINGTON, D. C., June, 1917.

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[1] Birge and Juday, Wis. Geo. and Nat. Hist. Sur., 1911, Bul. 22.
[2] Helland-Hansen, "Meddelelser om Oesteraylen," III, pp. 1–109 (1907); abstract, Wis. Geol. and Nat. Hist. Sur., 1911, Bul. 22, p. 63.
[3] Cummings, Bul. 104, Hyg. Lab., Wash., pp. 224, 229.
[4] Purdy, Hyg. Lab., Wash., Bul. 104, pp. 152, 190.
[5] Lebedinzeff, "Aus. der Fischzuchtanstalt Nikolsk," No. 9, pp. 113–136 (1904); abstract, Wis. Geol. and Nat. Hist. Sur., 1911, Bul. 22, p. 60.

Heating Houses With Gas. E. D. MILENER. (*American Gas Engineering Journal*, vol. cvii, No. 18, p. 393, November 3, 1917.)—As a producer of heat units on the generous scale requisite for such service as house heating, manufactured city gas has not in the past been able to compete with coal, and the householder has had to accept the inconveniences of the latter fuel. There are, of course, other economies than those of fuel cost gained by the use of gas, and latterly, in Baltimore, the Consolidated Gas, Electric Light and Power Company has demonstrated that fuel-gas house heating is possible by the maintenance of a house-heating service supplying 500 dwellings.

An efficient furnace is a prerequisite to success with gas fuel. Even with gas at 35 cents a thousand cubic feet and coal at $8.50 a ton, the average fuel cost of heating an entire house with gas will be at least 25 per cent. more than with coal, and to keep this difference from being greater it is necessary that the best equipment only be used and proper attention given to its operation. A three-story cottage equipped with a gas-fired steam-heating system consumed, during the eight months from October to May, 465,800 cubic feet of gas. The lowest monthly consumption, during October, was 23,700 cubic feet, and the highest, during February, was 88,700 cubic feet.

STUDIES IN ACTINOCHEMISTRY.*

BY

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It is also interesting to note the observations of Cohen and Wassiljewa,[116] that equilibrium is brought about in absence of light by submitting a mixture of hydrogen and chlorine to the catalytic action of charcoal.

They found, also, that if gaseous hydrochloric acid was passed through a quartz tube which was two centimetres from the lamp (a mercury quartz lamp), and this tubing was protected from all light, the gas was decomposed. If the quartz tube was replaced by glass no decomposition of the hydrochloric acid took place.

Russ,[117] in his paper on the action of the silent electric discharge on chlorine, after a description of experiments concludes that an active form of chlorine is produced by the silent electric discharge and by ultraviolet light, and that this action of chlorine will greatly diminish when the light or discharge is taken away. He noted the dependence of the activity on moisture, and pointed out the analogy between the effects of moisture on the activation of chlorine by the silent electric discharge and those in which activation was accomplished by means of light pointed out by Mellor,[118] Gautier and Helier,[119] and Bevair.[120] He believed that the action of the discharge was photochemical, because the effect was produced in a quartz chamber much better than in glass. He found that the charged chlorine held its activity for a long time, but would lose it on being heated or passed through glass tubing. This observation, made also by Bevan,[121] is important, as the phenomenon is exhibited by gases known to be electrically charged.[122]

* Concluded from page 636, vol. 184, November issue.

[116] *Loc. cit.*

[117] *Monatsch.*, **26**, 627–646 (1905).

[118] C. B. I., 1057 (1904).

[119] *Compt. rend.*, **124**, 1267 (1897).

[120] *Proc. Roy. Soc.*, **72**, 5, (1903).

[121] *Loc. cit.*

[122] See J. J. Thompson, "The Conduction of Electricity Through Gases."

In his experiments, Russ used benzene as a proving substance, and found that the maximum effect of sunlight on chlorine and benzene is localized in the ultraviolet portion of the spectrum.

In this connection it may be pointed out that Warburg[123] found that there was a maximum in ozone formation by the silent electric discharge, and that the laws of Faraday did not apply to the formation of ozone. He expresses the idea that the action of the silent electric discharge must be conceived as being photo- or cathodo-chemical in character.[124]

After several attempts to chlorinate acetic acid by electrolysis under various conditions, Schluederberg[125] concludes that, "while it is possible to chlorinate acetic acid electrolytically, yet from the standpoint of efficiency the results obtained are of a very unsatisfactory nature." Schluederberg conducted his experiments on a belief "that light causes a dissociation." Bancroft[126] considers that positive and negative chlorine are produced by dissociation caused by light, and that the dissociation effects of light can be duplicated electrolytically and that light and halogen carriers act in the same manner, but it has since been found that in toluene electrolytic chlorine substituted in the ring, and ordinary chlorine in the presence of sunlight in the side chain. This would indicate that the chlorine substituted in acetic acid is the same as that substituted in the side chain in toluene. Schluederberg designates this chlorine positive, in distinction to that which enters the ring of toluene and benzene, which is called negative. The positive chlorine is considered as replacing the hydrogen of the acid, which subsequently unites with the negative chlorine and forms hydrochloric acid. By this reasoning the postulate that dissociation effects of light can be duplicated electrolytically does not hold, and it is seen that their action can be duplicated electrolytically only when halogen carriers act in a different way from light. Ferric chloride, on the other hand, can be considered as dissociating into ferrous chloride and negative chlorine. This action can be duplicated electrolytically. With phosphorus pentachloride dissociation may occur into phosphorus trichloride and positive chlorine, thus accounting for its activity.

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[123] *Ann. Phys.*, 9, 781 (1902); *Ibid.*, 13, 464 (1904).
[124] See also Regener, *Ann. Phys.*, 20, 1033–1046 (1906).
[125] *J. Phys. Chem.*, 12, 583–589 (1908).
[126] *J. Phys. Chem.*, 12, 439 (1908).

Because of the small amount of chloracetic acid obtained Schluederberg believed that what was formed was due to ordinary chlorine discharged from the electode and dissolved in the acid, and not from negative chlorine set free from the anode.

The above considerations give us reason to believe that the action of light is to ionize the chlorine. Similarly to the manner in which the ionization of other gases by light, X-rays, or silent electric discharge takes place, in which cases the gases are known to contain free ions.[127] McClung describes two interesting experiments [128] which prove conclusively that the charged gas can be carried along a tube for some distance before it loses its charge.

CHLORINATION OF BENZENE.

Another reaction which is accelerated by light energy is that between chlorine and benzene. The effect of light on this reaction was reported first by Mitscherlich,[129] who formed chlorbenzene by allowing chlorine to act on benzene in the sunlight.

Willgorode [130] reported that benzene does not react in the dark with chlorine at any temperature up to the boiling-point of the solution under atmospheric pressure. In spite of his work, it is stated in several text-books and in the literature [131] that chlorine does react on boiling benzene in the dark. This latter view was prevalent until Slator,[132] followed by Goldberg,[133] proved the reaction between chlorine and benzene to be photochemical. In his work Slator [134] pointed out that the velocity of the reaction was directly proportional to the square of the chlorine concentration—a phenomenon which is pointed out by Goldberg [135] as an exception to the usual laws governing the velocity of photochemical reaction.

It may be noted, also, that Bodenstein and Dux [136] found that

[127] See J. J. Thompson, *loc. cit.*, and McClung, "Conduction of Electricity Through Gases and Radio-activity."

[128] Pages 61 and 92.

[129] *Pogg. Ann. Phys. u. Chem.*, **35**1 (5), 370–374 (1835).

[130] *J. Prakt. Chem.*, **34**, 264 (1886).

[131] Lesimple, *Lieb. Ann.*, **137**, 123.

[132] *Z. Phys. Chem.*, **45**, 513 (1903).

[133] *Z. wiss. Phot.*, **4**, 61–107 (1906).

[134] *Loc. cit.*

[135] *Loc. cit.*

[136] *Z. physik. Chem.*, **85**, 297–328 (1913).

the combination of hydrogen and chlorine was a reaction of the second order, the velocity being proportional to the square of the chlorine concentration.

Goldberg [137] points out the peculiar effects due to dispersion of light when the reaction between benzene and chlorine is carried out in a glass tube. He found that if concentric tubes were used, under the circumstances, the velocity of the reaction in the outer tube was less than in the inner tube, although the strength of the light is greater in the outer container than in the inner one. He calls attention to the concentration of the light following its dispersion by entrance into the outer vessel to account for these somewhat paradoxical results. The apparatus which he used for his further researches avoids the possibility of such peculiar effects by causing the light to pass through a flat piece of glass or quartz.

Goldberg found by plotting curves showing the concentration as a function of the time, velocity as a function of the time, and velocity as a function of the concentration, that the course of the reaction between benzene and chlorine could not be predicted by using the usual photochemical laws. He points out that, while with a small initial concentration the velocity diminishes with decreasing concentration, with high concentration it increases with decreasing concentration. He also found by experiment that in higher concentrations the phenomenon of self-acceleration was exhibited.

Goldberg, whose work was extensive on this phenomenon, showed that the extent of retardation in this reaction by the presence of oxygen was very marked with increasing concentration.

Luther and Goldberg [138] also found that the action of chlorine on benzene was greatly retarded in the presence of oxygen. They pointed out that this retardation probably would account for the reaction between chlorine and benzol in boiling solutions, as reported in text-books. Their experiments showed that there was little reaction in the dark even at high temperature, and they believe that the extreme sensitiveness of the reaction in the absence of oxygen makes it probable that the light of an ordinary laboratory is sufficient to bring about the reaction in a boiling solution. They believe that the formation of hexachlorbenzene in the ab-

[137] *Loc. cit.*

[138] *Z. physikal. Chem.*, 56, 43–56 (1906).

sence of catalyzers is a purely photochemical reaction. Hexachlorbenzene cannot be formed in the dark in the presence of alkalies.

Dyson and Harden [139] pointed out that the retardation by oxygen was characteristic of all photochemical gas reactions. This observation was confirmed by Luther and Goldberg.[140]

It is of interest to note that a patent was recently granted to Sparre and Masland [141] for apparatus to be used in chlorinating saturated hydrocarbons. The material is charged with chlorine in an opaque absorption chamber, then passed through a series of glass tubes in which it is exposed to a mercury vapor light.

Attention has already been directed to the unsuccessful attempts of Schluederberg to form chlorbenzene and chlortoluene electrolytically. Van Name and Maryott [142] also report experiments which indicate that anodichlorination of benzene is absent, and that the chlorination found was due to a catalytic action of lithium chloride used, whether the chlorine is liberated by the electric current or simply introduced by bubbling it through the solution.

CHLORINATION OF TOLUENE.

Referring to another reaction, the chlorination of toluene, which is accelerated by the action of light and offers some interesting features, Bancroft, [143] cites the work of Schramm,[144] who reported that chlorine was substituted in the side chain when it acted on toluene at 0° in the sunlight, and that of Cannizzaro,[145] who reported side-chain substitution when chlorine acted on boiling toluene, and says that it is probable that the latter method of preparation is a photochemical one.

Cohen, Davison, Blochey, and Woodmansey [146] studied variations in the conditions of the chlorination process of toluene. Their experiments were divided as follows:

Series 1 and 2: Chlorination above a layer of hydrochloric acid solution (D1.16) in the dark and in diffused sunlight.

[139] *J. Chem. Soc. Trans.*, **83**, 201 (1903).
[140] *Loc. cit.* See also Bodenstein and Dux, *Loc. cit.*, and Taylor, *loc cit.*
[141] *Loc. cit.*
[142] *Am. Jour. Sci.*, **35**, 153–170.
[143] *Loc. cit.*
[144] *Ber.*, **18**, 606 (1885).
[145] *Compt. rend.*, **41**, 517 (1855).
[146] *J. Chem. Soc. Trans.*, **87**, 1034 (1905); **97** (2), 1628–1636 (1910).

Series 3 and 4: Chlorination with moist chlorine in the dark and in diffused daylight.

Series 5 and 6: Chlorination with dry chlorine in the dark and in diffused daylight.

The toluene in all cases was heated to the boiling-point.

These authors report experiments in which the chlorine was exposed to the light of an arc lamp focussed on the wash bottle of sulphuric acid before it came in contact with the toluene; others where the chlorine was exposed to diffused daylight, the sulphuric acid being replaced by water; others where the light of an incandescent electric lamp was allowed to act on the chlorine while entering the toluene.

They conclude that the proportion of side-chain substitution products obtained is not attributable to the influence of chlorine previously exposed to light.

The authors also show by experiment that the influence of light on the ratio of distribution of chlorine is very pronounced in the case when the reacting chlorine was passed through concentrated aqueous hydrochloric acid in contact with toluene. The effect of illumination was to raise the proportion entering the side-chain substitution from 16 to 60 per cent. Where moist gas was passed direct into toluene the percentage of benzyl chloride formed was raised from 60 to 90. When, however, the dry gas is passed into dry toluene in the dark the proportion of substituted products obtained is so large that any considerable influence of light is excluded. The effect of light in this case is very slight, the proportion of benzyl chloride being increased from 90 to but 94 per cent. The authors found that in the dark the distribution of chlorine is very largely dependent on the amount of water present. They further found that electrolytic chlorine in the dark gave rise to a somewhat smaller proportion of benzyl chloride than chlorine which is obtained by the action of potassium permanganate on hydrochloric acid. The fact that the conditions were not identical, due to the hydrogen liberated at one pole, was noted, a possible explanation being that the benzyl chloride which dissolved in the hydrochloric acid was reduced by the hydrogen, thus accounting for the small proportion of the benzyl chloride in the product.

If the chlorination by electrolysis is carried on in the light,

the action is not sensibly different from that which occurs when ordinary chlorine is used.

The authors state that, "from a consideration of all the observations relating to the chlorination of toluene, it appears to be established that side-chain substitution is favored by light, rise of temperature, and absence of moisture."

They also conclude that the mechanism of the process of chlorination is of the same kind as that of bromination, and suggest that the more extensive observations relating to the bromination of toluene may be utilized in the elaboration of a general theory of halogenation.

There are two essentially different views in explanation of the various observations relative to the bromination of toluene under many varying conditions studied by Holleman, Polak, Van der Loan, and Envas.[147] The essential point of the one advanced by Bruner is that side-chain substitution is due to molecular bromine, whereas nuclear substitution is effected by bromine atoms or ions which result from the dissociation of the bromine molecules. The hypothesis is strengthened by the velocity measurement made by Bruner and Blusha.[148] The action of carriers is thought to be due to formation of compounds of bromine which undergo dissociation with the production of bromine atoms or ions in much greater concentration than in that which exists in a pure solution of bromine.

Bruner's theory is, in its essential characteristics, adopted by Bancroft, who gives a review of the subject of the chlorination and bromination of toluene and benzene in his third article on the "Electro-chemistry of Light."[149] He adds that the nuclear substitution takes place only when negative bromine ions are in excess of the positive ions, a condition brought about by the partial combination of the positive bromine ions with molecular bromine to form complex positive ions; for example, Br_3.

The second view, that of Holleman, is based on the supposition that substitution in the side chain is due to the molecular bromine, while that in the nucleus is brought about by hydrogen perbro-

[147] Proc. K. A. Kod, *Wetensch. Amsterdam*, **8**, 512 (1905); *Rec. Tra. Chem.*, **27**, 435 (1908). See also Branerad Dlusha, *Bull. Acad. Sci. Cracow*, **693** (1907), and Jackson and Field, *Amer. Chem. Jour.*, **2**, 10 (1881).

[148] *Loc. cit.*

[149] *J. Phys. Chem.*, **12**, 417 (1908).

mide.[150] He points out that this compound is most abundant at low temperature where low concentration of bromine is employed, which is the condition under which bromine enters the nucleus. It was noted, also, that the addition of acetic acid or nitrobenzene probably acts by changing the concentration of the bromine.

Cohen, Davison, Blochey, and Woodmansey[151] say that "both of these views offer a plausible explanation of certain facts, but the view that nuclear substitution is due to halogen in the form of polyhalogen compounds appears to be more acceptable." They refer to the diminution in the relative amount of nuclear substitution with rise of temperature and with diminishing concentration of the halogen as being both consistent with this theory, because they both favor dissociation of the polyhalides. They further refer to the increase in the percentage of nuclear substitution product when certain solvents are added as being in accord with the fact that these solvents facilitate the formation of polyhalogen compounds.

It is suggested as possible that the relative stability of polyhalogen compounds in nitrobenzene solution is connected with the ionizing power of this solvent. Attention is called to the slight conductivity demonstrated by Davison and Gwaler,[152] and Davison and Jackson.[153] Other solvents which favor the formation of polyhalogen compounds and increase the relative amount of nuclear product in the bromination of toluene also yield solutions which have a high electrical conductivity.

Cohen, Davison, Blockey, and Woodmansey[154] say that although there is no direct evidence to show that the nuclear substitution effect is conditioned by the ionization, yet these facts would seem to indicate that halogen in the form of polyhalogen ion is especially active in this respect.

These authors point out the following facts, which are difficult to reconcile with the ionic theory: That Bruner[155] found that solutions of bromine and iodine in moist nitrobenzene were conductors of electricity, while Brunner and Galechi[156] found that solutions of chlorine in nitro-benzene do not conduct elec-

[150] HBr_n.
[151] *J. Chem. Soc. Trans.*, 97, 1623–1636 (1910).
[152] *J. Chem. Soc. Trans.*, 81, 525 (1902).
[153] *Ibid.*, 93, 2063 (1908).
[154] *Loc. cit.*
[155] *Bull. Acad. Sci. Cracow*, 731 (1907).
[156] *Zeit. Electrochem.*, 16, 204 (1910).

tricity, and yet the processes of chlorination and bromination appear to be effected in a similar way when the conditions of the two processes are similarly altered.

Neither theory will account for the fact that water in the toluene increases the relative proportion of the nuclear substitution products. Observations on the conductivity of toluene solutions of moist and dry chlorine show no difference that would account for the observed action on the "chlorine ionization theory," since the action of moisture opposed that of light.

In connection with the theory of carriers, that their action is due to concentration of halogen ions as a consequence of the formation of more highly ionized carrier-halogen compounds, it is stated that it is not supported by any experimental evidence, so far as these authors are aware. It is pointed out, on the other hand, that if such "carrier-halogen compounds" are themselves of the nature of perhalogen compounds, or if they are capable of combining with further quantities of halogen to form such perhalogen derivatives, the formation of nuclear substitution products in the presence of carriers is explicable in terms of the polyhalogen theory without the necessity of formulating any additional electrical hypothesis. "From a consideration of the valency relationships of the various substances which serve as carriers it seems likely that all these substances are capable of forming dissociating halogen addition compounds which belong to the polyhalogen type."

Cohen, Davison, Blockey, and Woodmansey [157] called attention to a change in color when moist chlorine acted on toluene in the presence of light. The toluene gradually assumed the yellow color of chlorine. If hydrochloric acid gas was passed in simultaneously, the yellow color disappeared, but reappeared when the hydrochloric acid was cut off. In the dark the yellow color was retained in the presence of hydrochloric acid. In some cases the color is retained after washing the product until free from hydrochloric acid and chlorine. They suggest that a small quantity of a yellow-colored substance was formed. This phenomenon was to be the subject of further research.

Haussemann and Beck [158] made the interesting observation that side-chain substitution of chlorine in nitrotoluene was greatly

[157] *J. Chem. Soc. Trans.*, 97, 1623–1636 (1910).
[158] *Ber.*, 25, 2445 (1892).

facilitated by the presence of sulphur. Sulphur thus appears to act differently from the usual carriers, such as ferric chloride, molybdenum chloride, antimony chloride, iodine chloride, pyridin, and aluminum-mercury couple, which bring about nuclear substitution.

The boiling-points of the chlorine derivatives of toluene are given by Rosenthaler.[159]

EFFECTS OF CHEMICALLY ACTING RAYS ON NITROGEN COMPOUNDS WITH SPECIAL REFERENCE TO TRINITRO-TOLUENE.

There are several references in the literature to the action of light on nitrogen compounds, its action on the nitro-explosives being particularly interesting and, in view of the existing conditions in Europe, of no small importance.

Abel [160] reported experiments on the action of light on gun-cotton conducted by him about 1867. A sample very carefully washed and dried was exposed in a closed vessel to diffused sunlight for three years. A piece of litmus paper enclosed with it turned red in three months and was bleached within twelve months. After twelve months the cotton possessed a faint but decided cyanic odor. No nitrous vapors were perceptible at any time, though the odor was apparent during the latter part of the experiment. Although the gun-cotton showed no change in explosive power, strength of fibre, or other noticeable properties, the above observations indicate decomposition. The results obtained up to that time by exposure of gun-cotton to light were reported to be as follows: Exposure to strong daylight and to sunlight, either in the open or in confined spaces, for a few days (two or three), develops in the gun-cotton a very faint aromatic odor; and if litmus paper is allowed to stand in close contact with the confined material it acquires a rose-colored tinge similar to that produced by carbonic acid, and recovers its original color after brief exposure to air. If, after exposure to light in open air for some days, the gun-cotton is placed in the dark, in containers which are not air-tight, the odor gradually becomes less distinct. If, however, the packages containing the gun-cotton are air-tight, the odor and action upon litmus do not increase during storage for several years. On exposure for protracted

[159] "Der Nachweis organischer Verbindungen," 1914, p. 464.
[160] MacDonald, *Arms and Explosives*, 17, 150–152 (1909).

periods to daylight, with free excess of air, gun-cotton speedily loses all odor and power of affecting litmus. If exposure to diffused daylight in confined spaces be continued the first effects of the action of light are, of course, retained, but no evidences of increased action have been observed. The very faint acid reaction found in the early stages of decomposition was not always evident later, probably, it is thought, because the acid was neutralized by the small quantities of earthy carbonates present in the cotton. On exposure of the material in an air-tight space to the action of sunlight or strong daylight there appeared, after a time, much greater evidence of change than that already described. The acidity gradually became more decided, the odor increased, the presence of nitrous oxide was apparent, and litmus paper confined in the vessel with the cotton became bleached in three or four months.

Reference is made to the work of DeLuca, who reported apparent change in the gun-cotton after very short periods of exposure to light (one day or several days). These results, however, are at variance with those reported by MacDonald.[161] Experiments showed that dry gun-cotton undergoes very slight decomposition when exposed to strong daylight in closed vessels, either containing air or exhausted. In about three years the explosive value was found to have diminished. This was attributed to the formation of lower cellulose products from the trinitro-cellulose. It was noted that on washing the cotton with dilute alkali the residue had useful explosive properties and exhibited no greater tendency to change than the original material.

The change in sunlight was found to be more rapid in a moist atmosphere, and it was further found that the rate of decomposition was dependent on the purity of the product.

It may be noted that when gun-cotton is heated gradually to 204° or 205° [162] it becomes dark brown, quite friable, and is deprived of its explosive properties.

According to Kassel,[163] nitro bodies are reduced to amido bodies by the action of light in the presence of alcohol. The part played by alcohol has not been established.

Berthelot and Gaudechon [164] showed that various kinds of

[161] *Loc. cit.*
[162] MacDonald, *loc. cit.*
[163] *J. Suisse de Chimie. Pharm.*, 47, 722–724 (1909).
[164] *Compt. rend.*, 153, 1220–1223 (1911).

smokeless powders were decomposed by exposure to ultraviolet rays in a manner similar to that due to the influence of natural agents—heat, humidity, and action of air. Samples of ten different varieties of powder were confined in quartz tubes over mercury in atmospheres of different gases and exposed to the rays from a mercury quartz arc. The temperature was kept below the point at which the powder under test would decompose. They all evolved carbon dioxide, carbon monoxide, nitrogen, nitrous oxide, and nitric oxide. These observers noted the absence of hydrogen and methane, which are products always found when explosion takes place. They point out that the acceleration of spontaneous decomposition of powder when subjected to the action of ultraviolet rays furnishes the elements of a new and precise method of investigation. Such a method would serve as an admirable substitute for the widely used heat tests for the control and complete examination of the stability of powder.

These authors[165] exposed different grades of powders in atmospheres of different gases to ultraviolet light from a mercury quartz lamp. They found that oxygen was absorbed and converted into carbon dioxide. Hydrogen was converted into CH_2 (?) and water. Carbon dioxide was absorbed at 25° to 40°, but at 75° more carbon dioxide was evolved from the powder. They pointed out that the decomposition of these powders by light yielded the same products as slow decomposition due to heat, moisture, etc. The presence of atmospheric nitrogen did not prevent the evolution of nitrogen from the powders, but in the presence of carbon dioxide there was no carbon dioxide evolved. Nitro-cellulose powders suffered no change in appearance, but change in color and exudation of nitroglycerin resulted with powders containing nitroglycerin. These authors also found that, while picric acid was slightly affected by the light, ammonium picrate was not. They called attention to the possible effect on the results of those stability tests in which the explosive is heated in carbon dioxide, and recommend nitrogen in its place. One such test is the "Will Test," which is extensively used in Germany.

Wöhler[166] showed that on exposure to sunlight or to ultra-

[165] *Compt. rend.*, 154, 201–203, 514–517 (1912).

[166] *Z. org. Chem.*, 24, 2095 (1911); also see Wöhler and Krupko, *Ber.*, 46, 2045–2057 (1913).

violet light the nitrides were very quickly decomposed into the metal and nitrogen. The metal he was able to detect microscopically, and the presence of nitrogen by means of a manometer.[167] While these substances are the same as are produced by explosion, Wöhler claimed that the decay caused by light took place only at the surface, the under layers being protected by the opaque layer thus formed, and that, in consequence, the explosive properties of the substance were practically unimpaired for commercial purposes.

The color that is produced by the action of light on the nitrides Wöhler attributed to the liberation of the free metal in colloidal form. Incidentally, he draws a comparison between this conduct of the nitrides and the similar conduct of the silver halides, and attributes the color produced in silver chloride by the action of light to the liberation of metallic silver in colloidal form, rather than to the production of subhalides.

Neitzel[168] refers to the work of Wöhler, stating that it is still conceivable that there is a light-sensitiveness in the under layers of nitride. He further points out that the dangerous auto-decomposition of large crystals which can take place even under water may be attributed less to the forces postulated by Wöhler "in his crystal tension hypothesis" than to the influence of light. He also calls attention to the necessity for confirmation of Wöhler's observation that the detonating power is not changed by the influence of light. Neitzel refers to the susceptibility of the nitrides to action of light as a possible disadvantage of their use in detonators.

Another explosive which has been the subject of experiment is synthetic trinitrotoluene. According to Molinari and Quartier,[169] this substance remains completely unaltered in dry or damp air in the dark. When exposed to bright daylight, however, it becomes brown slowly on the surface. This brown product was investigated by Doctor Milani, of the Societa Italiana Prodotti Explodenti. The original substance was solid at 80.4° and left 0.03 per cent. residue in acetone solution. By longer illumination, with frequent shaking, the solidifying point sank first to 80°, then gradually to 79.6°. The product left from 0.05

[167] *Z. Aug. Chem.* (1911–1912).
[168] *Z. ges. Schiess-Sprengstoffw.*, **8**, 211 (1913).
[169] *Ibid.*, **8**, 405–407 (1913).

per cent. to 0.10 per cent. insoluble residue in acetone solution. Molinari and Giua showed that the melting-point of trinitrotoluene was lowered to 74° by exposure to daylight for three months in an open flask, and that if the flask was evacuated the browning was decidedly less and the melting-point was lowered only 0.6°.

In view of the similarity in action between heat and light, referred to above, in connection with the action of light in the formation of chlorine compounds, it is interesting to note the observations of Verola.[170] This investigator found that there was a decomposition of trinitrotoluene at temperatures much below the point at which it would deflagrate in air. He also noted that a previous heating of trinitrotoluene lowered its melting-point. On heating a sample that had an original melting-point of 80.75° for five hours at 180° the melting-point was reduced to 78°; two and one-half hours at 217.5° gave a product having a melting-point of 59°. Continued heating at 130° for one hundred hours had no effect, while 80 hours' heating of the same sample at 150° reduced the melting-point to 80.25°, and 177 hours' heating at 150° gave a further reduction to 79.9°. He says that it is evident that the explosive is very stable at 130°, decomposition beginning at about 150° and increasing rapidly as the temperature rises. He considers trinitrotoluene to be perfectly stable at ordinary temperatures.

Those who are interested in the true melting-point of trinitrotoluene are referred to the work of Comey,[171] who found it to be between 80.5° and 80.6°, and to the later work of Rintoul,[172] who gives it as lying between 80.8° and 80.85°.

Particular attention in this work has been paid to the variation in melting-point of trinitrotoluene because of its importance in grading the product with respect to its purity.

It was suggested that additional information relative to the effect of light on trinitrotoluene would be of value. Before reporting experiments on this research, however, it would seem to be of advantage to call attention to the effect of light on other nitrogen compounds.

The fact that sunlight will cause decomposition of nitric acid

[170] *Ibid.*, 7, 97.
[171] *J. Ind. Eng. Chem.*, 2, 103 (1910).
[172] *J. Soc. Chem. Ind.*, 34, 60-61 (1915).

has been known for a long time. The first report of systematic study of the problem did not, however, appear until 1898. In that year Berthelot [173] showed that the decomposition products of nitric acid produced under the influence of light are the same as those obtained when the anhydrous acid is heated in tubes to 100° in the dark for some hours, namely, oxygen, nitrogen peroxide, and water. This reaction, which may be represented as follows:

$$4HNO_3 = 2H_2O + O_2 + 2\ N_2\ O_4$$

was found by him to be non-reversible. A little earlier in the same year Veley and Manley [174] pointed out that the light appeared to act only on the vapor and not on the liquid. This interesting observation was confirmed later by Reynolds and Taylor.[175] Reynolds and Taylor,[176] contrary to the observation of Berthelot,[177] found the reaction to be reversible, the products of decomposition of nitric acid by light recombining in the dark. This was in accordance with the results obtained in the study of other reactions in which nitric acid took part. They illustrated the rate of decomposition and recombination by a series of curves. They further proved that pure anhydrous nitric acid decomposes very slowly in the dark, giving the same products of decomposition as are found in the light.

That nitrates also are decomposed by light was found by Thiele,[178] who obtained 24 milligrammes of N_2O_3 on exposure of 100 cubic centimetres of a one-tenth normal solution of potassium nitrate in a quartz flask to the rays from a mercury quartz lamp.

Later, Berthelot and Gaudechon [179] found that, on exposure to ultraviolet rays from a mercury quartz light, solutions of ammonia placed three to six centimetres from the lamp were oxidized in the presence of pure oxygen or air to nitrites. They state that nitrates were in no case formed. Ammonium salts

[173] *Compt. rend.*, 127, 143 (1898).
[174] *Phil. Trans.*, 191, 365 (1898).
[175] *J. Chem. Soc. Trans.*, 101, 131–140 (1912); *Proc. Chem. Soc.*, 27, 306 (1911).
[176] *Loc. cit.*
[177] *Loc. cit.*
[178] *Ber.*, 40, 4910.
[179] *Compt. rend.*, 152, 522–542 (1911).

were also oxidized to nitrites, the action being slower in the case of sulphates and chlorides than in the case of carbonates.

It is interesting to note in this connection that the nitrates found in meteoric waters are attributed to electric discharges taking place in the air.[180]

It is also interesting to note in this connection that Thompson[181] found ammonia was strongly ionized by ultraviolet light. It may be added that Thompson observed that the ultraviolet rays are absorbed to such an extent by passage through three millimetres of air at atmospheric pressure that they lose their ionizing energy almost entirely. Berthelot and Gaudechon[182] also report the formation of formamide from carbon monoxide, and ammonia gas.

Baker[183] found that B. p-nitrophenol, a yellow compound, slowly turned red on exposure to sunlight.

Kailan[184] found that the oxidation of o–, m–, and p–nitrobenzaldehyde and benzaldehyde was accelerated by ultraviolet light.

Benrath[185] found that on dissolving various aliphatic bodies in dilute nitric acid, containing a little ferric nitrate, and exposing to sunlight, nitrous oxide, a little carbon dioxide, formaldehyde, and large quantities of hydrocyanic acid were formed.

Bakunin[186] reported that the precipitate formed by exposing to light ethereal solutions of the phenylnitro-indones had explosive properties.

Light also has an effect on certain of the alkaloids and similar nitrogen-containing substances. This branch of the subject will be treated under the heading "The Effect of Light on Nicotine."

In considering the action of light on the nitroderivatives of benzene and its homologues it is well to note the observation of Suida,[187] who found that benzene was scarcely affected by the action of light, but that the susceptibility rapidly increased with the number of methyl groups present.

[180] Müntz and Laine, *Compt. rend.*, **152**, 167 (1911).
[181] *Proc. Camb. Phil. Soc.*, **14**, 417.
[182] *Compt. rend.*, **150**, 1690–1693 (1910).
[183] *Proc. Chem. Soc.*, **27**, 158.
[184] *Monatsh.*, **33**, 1305–1327.
[185] *J. prakt. Chem.*, **84**, 324–328.
[186] *Rend. Accad. Sci. fis. mat Napoli*, **17**, 375–378.
[187] *Monatsh.*, **33**, 1255–1258.

Ciamician and Silber [188] confirmed the work of Suida, that benzene is not affected by oxygen and water, in the presence of light. Berthelot and Gaudechon [189] state that ultraviolet light has no effect on benzene. They further point out that in other cyclic bodies (pyrrole, furfurol, pyridine, and a few alkaloids) their behavior is in accordance with the well-known stability of the aromatic nucleus toward heat, light, and chemical reagents.

In 1906 Regener [190] showed that ammonia, nitrous oxide, and nitric oxide were decomposed by ultraviolet rays of short wavelength. In his paper he refers to the work of Berthelot,[191] who found that nitric oxide was reduced to oxygen and nitrous oxide, under the influence of the silent electric discharge. Here, again, we have evidence of the similarity of chemical action produced by light and by the silent electric discharge referred to above in the discussion of the action of light on chlorine. Further consideration of these phenomena may add weight to the hypothesis of Warburg,[192] that the action of the silent electric discharge was dependent on the ultraviolet rays present in the discharge.

Berthelot and Gaudechon [193] found that ammonia could be decomposed by ultraviolet light, but that it could not be similarly synthesized from the elements, hydrogen and nitrogen. Coehn and Prigent [194] found that ammonia was completely decomposed by ultraviolet light. Davies [195] found that the reaction between nitrogen and hydrogen under the influence of the silent electric discharge was reversible. Regener [196] showed that ammonia was decomposed by the silent electric discharge and also by the ultraviolet light.

The reversibility of the reaction between nitrogen and hydrogen was also pointed out by Smiths and Aten,[197] who reported the synthesis of ammonia from its elements under the influence of the rays from a quartz mercury light. Coehn [198] and Coehn and

[188] *Ber.*, **46**, 417–422.
[189] *Compt. rend.* **152**, 262, 376–378 (1911).
[190] *Ann. Phys.*, **20**, 1033–1046 (1906).
[191] *Compt. rend.*, **82**, 1360 (1876).
[192] *Loc. cit.*
[193] *Compt. rend.*, **156**, 1243 (1913).
[194] *Z. Electrochemie*, **20**, 275–278 (1914).
[195] *Z. physik. Chemie*, **64**, 657 (1908).
[196] *Berl. Akad. Ber.*, 1228 (1904).
[197] *Loc. cit.*
[198] *Jahrb. Radioakt. Elektronik.*, **7**, 577 (1911).

Prigent [199] are inclined to doubt the validity of the results obtained by Smiths and Aten, pointing out that the waves of short wave-length, which would be effective in this reaction, are absorbed by quartz. They also point out that Warburg [200] showed that the percentage of ultraviolet rays absorbed by the mixed gases, nitrogen and hydrogen, was about the same as by pure ammonia. In this connection it is interesting to note the observation of Davies,[201] that the decomposition of ammonia, under the influence of the silent electric discharge, is independent of the discharge.

Berthelot and Gaudechon [202] report that ultraviolet rays produce no appreciable effect on air or mixtures of oxygen and nitrogen, but that nitrous oxide alone, or mixed with oxygen and nitric oxide, is decomposed with the formation of free nitrogen and nitrous and nitric acids.

Other compounds which contain nitrogen that are influenced by ultraviolet light were reported by the same observers. They [203] found that cyanogen in the presence of oxygen was practically completely oxidized to carbon dioxide and nitrogen. Cyanogen in the absence of oxygen was found by them [204] to form paracyanogen. They also found that a mixture of ammonia and oxygen yields nitrogen and water, and that ammonium nitrate was reduced to nitrogen.

Ciamician [205] reported the synthesis of complex mixtures when hydrochloric acid acted on acetone in the presence of light.

Berthelot and Gaudechon [206] also found that urea decomposed under the influence of ultraviolet light, evolving seven volumes of carbon dioxide, 65 of hydrogen, and 28 of methane; an aqueous solution of urea gave 84 volumes of hydrogen and 16 of methane. The residual solution was found to possess reducing properties, and to contain ammonia and ammonium carbonate. By treating aqueous solutions of ammonia with air or oxygen in the presence of ultraviolet light Berthelot and Gaude-

[199] *Loc. cit.*
[200] *Berl. Akad. Ber.*, 746 (1911); 216 (1912).
[201] *Loc. cit.*
[202] *Compt. rend.*, 150, 1517–1520 (1910).
[203] *Compt. rend.*, 150, 1327–1329 (1910).
[204] *Compt. rend.*, 151, 1169–1172 (1910).
[205] See Kassel, *loc. cit.*
[206] *Compt. rend.*, 151, 478–481 (1910).

chon [207] obtained nitrous acid. Ammonium salts gave nitrites. They state that nitrogenation of various substances has been accomplished. They point out that the transformation of organic nitrogen to ammoniacal nitrogen is the first stage of nitrogenation of urea by ultraviolet rays, as is the case when nitrogenation is caused by the enzymes. They further found that nitrates could be reduced to nitrites. They point out the analogy between the reduction of ammonium nitrate to nitrogen under the influence of ultraviolet light, referred to above, and the reduction produced by heat. They refer to the observation of Lombard,[208] that potassium nitrate was reduced to potassium nitrite during sterilization of water by ultraviolet rays.

Ciamician,[209] in an address before the Société de Chimie de France, reported an unsuccessful attempt to synthesize acid amides from hydrocyanic acid by the action of light. Although the attempt failed, he states that the investigation is to be continued.

EFFECTS OF LIGHT ON NICOTINE SOLUTION.

It has been known for some time that solutions of nicotine change in strength with age when stored under different varying conditions. Of the several factors which might have an effect on these changes, that of the action of light on alkaloids has been the subject of very little study. Inghilleri [210] reports the synthesis of alkaloidal bases by the action of sunlight on a mixture of formaldehyde, concentrated aqueous ammonia, and methyl alcohol, which was confined in a sealed tube and left exposed to sunlight for seven months. Several products having basic properties and giving characteristic alkaloidal reactions were isolated. One of these, a crystalline substance, was identified as having the formula $C_6H_8N_2O$. The author gives distinguishing properties for this compound.

Sernogiotto and Hoschek,[211] in a paper entitled "Supposed Chemical Changes in Light," repeated the work of Inghilleri, but did not obtain similar results. They found that when formaldehyde and water are exposed to light practically no methyl

[207] *Compt. rend.*, **152**, 522–524 (1911).
[208] *Bull. Soc. Chem.*, No. 6, vii, viii (1910).
[209] *Bull. Soc. Chem.* (4), 3–4, i–xxvii, August 5.
[210] *Z. phys. Chem.*, **80**, 64–72 (1912).
[211] *Ibid.*, **90**, 437–440 (1914).

alcohol is formed. When formaldehyde and methyl alcohol are exposed methylal is produced, but no methyl formate, and that a mixture of formaldehyde, methyl alcohol, and ammonia yields hexamethylenetetramine, which they think probably is Inghilleri's new alkaloid.

In the same year Paterno and Maselli [212] reported the photo-synthesis of a new alkaloid from acetophenone and ammonia. The reagents were put in a closed tube and exposed to light for several months. A crystalline compound which was formed was found to have the composition indicated by the formula $C_{18}H_{18}N_2$. The authors describe the properties of this product in detail. Other than these researches, little can be found, excepting that which relates to the absorption effects of light produced by certain alkaloids in solution.

Paterno,[213] in his conclusion to a series of papers on the syntheses in organic chemistry by means of light, states that the formation of organic nitrogen compounds in indefinite amounts by the reduction of nitrates in the light in the presence of organic substances may be a fruitful field for research; he refers to the synthesis of photo-acetophenine and its analogues, and suggests that the possibility of introducing into vegetable alkaloids of great physiological activity complex lateral chains is capable of having great pharmacological importance.

Just recently, Ciamician and Silber,[214] who have done considerable work on the chemical action of light and different types of substances and different types of reactions, reported the auto-oxidation of nicotine and piperidin under the influence of light. Their experiments on nicotine were carried out as follows:

Twelve grammes of nicotine in 100 c.c. of water was placed in each of three five-litre flasks with oxygen and left in the light from May to November. The solution became a deep yellow, its reaction faintly acid, and the oxygen was almost completely used up. After diluting the contents of the flasks, an excess of barium carbonate was added and the product distilled with steam. Both the distillate and residue were examined. In the distillate were found unchanged nicotine, a small quantity of

[212] *Gazz. Chim. Ital.*, **42**, 65–75 (1912).
[213] *Gazz. Chim. Ital.*, **44**, 463–475 (1914).
[214] *Ber.*, **48**, 181–187 (1915).

ammonia, and methyl amine. From the residue there was isolated a large quantity of a product having the same composition as the oxynicotine of Pinner and Wolffernstein,[215] and Beilstein,[216] but a different melting-point for its picric acid salt and nicotinic acid. They say, in conclusion, that the auto-oxidation of nicotine under the influence of light furnishes, besides a tar-like product as a principal product, oxy-nicotine, which by further oxidation yields nicotinic acid and methyl amine. The reactions involved can be represented thus:

$$\underset{\text{Nicotine}}{C_{10}H_{14}N_2} \rightarrow \underset{\text{Oxy-nicotine}}{C_{10}H_{14}ON_2} \rightarrow \underset{\text{Nicotinic acid}}{(C_5H_4N)COOH} + \underset{\text{Methyl amine}}{HN_2.CH_3}$$

Dobbie and Fox [217] made a study of the relation between the absorption spectra and constitution of piperine, nicotine, cocaine, atropine, hyoscyamine, and hyoscine, and confirmed a previous conclusion,[218] that the absorption spectra of the alkaloids containing reduced and unreduced nuclei are the same as those of unreduced nuclei.

Michand [219] investigated various inorganic and organic substances with the object of noting their behavior toward ultraviolet light, and found that certain of the alkaloids do not reflect ultraviolet rays. He suggests a possible relation between this property and physical and chemical properties and possible application to analytical chemistry.

Gompel, Marcel, and Henri [220] report a quantitative study of the absorption of ultraviolet rays by alkaloids, and have applied a method for quantitative determination of alkaloids in body fluids and tissues by means of the ultraviolet absorption spectra to alkaloids of the piperidine and pynolidine group.

These absorption effects are referred to because of their connection with the principle that when light is absorbed it tends to produce a chemical change.

Berthelot and Gaudechon [221] report experiments on the

[215] *Ber.*, **24**, 64 (1891); **25**, 1428 (1892); **28**, 460 (1895); **34**, 2412 (1901).

[216] IV, 858.

[217] *Proc. Chem. Soc.*, **29**, 180; *J. Chem. Soc.*, **103**, 1193–6.

[218] Cf. Dobbie and Lauder, *C. A.*, **5**, 3563 (1911), and Dobbie and Lauder, *C. A.*, **6**, **1284** (1912).

[219] *Arch. Sci. Phys. Nat.*, **33**, 498; *Sci. Am. Sup.*, **75**, 5 (1913).

[220] *Compt. Rendu. Soc. Biol.*, **74**, 1066–1068; *Compt. Rendu.*, **116**, 1541–1544.

[221] *Compt. rend.*, **152**, 376–378 (1911).

"Comparative Action of Ultraviolet Rays on Organic Compounds of the Straight Chain and Cyclic Structure." Among the substances studied by them were pyridine and nicotine. They state that the untraviolet rays do not produce any gases with any of the bodies studied; that there was no change in color, and no visible alteration. They say that the results are different with addition compounds in which the double bonds of the nucleus have disappeared. They call attention to the fact that certain bodies such as hexahydrobenzene offer intermediate properties between aliphatic hydrocarbons and aromatic hydrocarbons. They observed that piperidine (hexahydropyridine) is decomposed by ultraviolet rays with formation of pure hydrogen. The pyridine nucleus has alternate single and double bonds which form a stable compound, while the piperidine nucleus has single bonds, forming a compound unstable toward the action of light. The authors, however, do not give the source of the light used, the distance from this source, or the length of time of exposure to the light.

HYDROGENATION OF OLEIC ACID BY LIGHT AND ELECTRIC DISCHARGE.

One of the interesting problems of chemistry has been to change the unsaturated hydrocarbons into saturated compounds by direct addition of hydrogen. A special case of such a transformation has been of particular interest because of the great commercial value of some of the products formed by hydrogenation of fatty oils. As an illustration of a decided change in the physical properties of an oil may be cited the change produced in cotton-seed oil by hydrogenation, the untreated oil being liquid at ordinary temperatures, while the treated oil is a solid at ordinary temperatures. An example of a pure chemical substance which undergoes a similar change in physical properties is oleic acid, which by hydrogenation is converted into stearic acid.

There are many successful methods for hydrogenation of the unsaturated acids, most of them requiring the use of metal catalyzers. Several methods have been proposed which involve electrolytic processes, and the use of light has been proposed in still other methods. Particular attention is called to the references hereafter mentioned which describe methods employing electricity and light.

The possibility of the use of electricity to bring about the

combination of hydrogen with oleic acid was suggested by Weinech.[222]

Later, Kuess [223] attempted to apply the electric current in conjunction with steam distillation of fatty acids. Magnier, Bragnier, and Tissier,[224] attempted the hydrogenation of oils and fatty acids by nascent hydrogen produced by electrolysis.

Later, Hemptinne [225] reported satisfactory results by making use of a method in which the fatty acid was brought in contact with hydrogen in the presence of a silent electric discharge.

Hemptinne performed experiments using several types of apparatus. The first experiments were done with an apparatus resembling an ozonizer, the current being supplied by a Ruhmkorff coil. Later, experiments were performed using a modified form of apparatus and a Tesla coil.

An attempt was made by Hemptinne [226] to discover a quantitative relation between the quantity of substance transformed and the intensity of the current. It was found, however, that there is not always a proportionality between the quantity of substance transformed and the intensity of the current. For a given intensity of current the quantity transformed reached a maximum, which varied with the pressure for a definite size discharge space.

It was pointed out that it was necessary for the current to act simultaneously on both liquid and gas to obtain satisfactory results. He concludes, from a research made on the influence of polarity, "that the action is independent of the electric particles of one or the other signs."

Hemptinne lays great emphasis on the observation that there is no direct proportionality between the intensity of the current and quantity of material transformed. "But," he says, "if one admits that the passage of the electricity does not interfere with the electric particles, it is necessary to conclude that these play only an indirect rôle in the phenomena." "This," he adds, "is not the same as in electrolysis of liquids, where there is always

[222] *Osterr Privil.*, 10, 400, July 19 (1886); fr. Ellis, "Hydrogenation of Oils," 13.

[223] *Chem. Ztg.*, 618 (1896).

[224] British Patent 3363, 1900; German Patent 126,446 October 3, 1899, and German Patent 132,223; Ellis, *loc. cit.*

[225] *Bull. Soc. Chem. belg.*, 26, 55-63 (1912); U. S. Patent 797,112, August 15, 1905, fr. Ellis, *loc. cit.*

[226] *Loc. cit.*

parallelism between chemical activity and the number of ions." Because of the complicated nature of the action produced by prolonged use of the current he believes it is impossible to draw positive conclusions.

Hemptinne found that the yield was dependent upon a great number of conditions, and called attention to the differences in yield which were functions of the period of vibration of the current, current density, pressure of the gas, temperature of the liquid, and space through which the discharge passed.

In view of the observation of Russ,[227] which indicates that the action of the silent discharge in accelerating the reactions between chlorine and benzene is due to light rays, it is suggested that the effects brought about with the apparatus used by Hemptinne would be greatly intensified if an ozonizer having one quartz plate instead of glass were used.

Marie [228] was able to reduce aconitic acid to tricarballylic acid, and cinnonic acid to phenylpropionic acid by electrolysis of an acid solution of a sodium salt of the acid to be reduced. There was no difference in the yield when different metals were used as cathode.

Petersen [229] reported a method for obtaining stearic acid from oleic acid by means of an electric current between nickel electrodes placed in an alcoholic solution of oleic acid to which a mineral acid had been added; as, for example, sulphuric or hydrochloric acid. Petersen tried also other cathode materials than nickel, and found that the results were no more satisfactory with platinum, lead, zinc, or mercury as cathodes. Less satisfactory results were obtained by an attempt to obtain an increased yield by conducting the electrolysis in alkaline aqueous and alkaline alcoholic solutions.

A year later Böhringer and Sohne,[230] working on the same principle as did Petersen, reported better results with other electrodes, especially cathodes of platinized platinum and also palladium electrodes covered with palladium black.

Utesher [231] uses both a silent discharge and a catalytic agent

[227] *Monatsch.*, **26**, 627–646 (1905).
[228] *Compt. rend.*, **136**, 1331–1332 (1903).
[229] *Z. Elektrochem.*, 549–553 (1905).
[230] German Patents 187,788, 189,332 (1906). Ellis, *loc. cit.*, p. 5.
[231] British Patent 20,061, fr. Ellis, *loc. cit.*, p. 33; German Patents referred to in *Seinfen Ztg.*, **40**, 851 (1913).

in the saturation of an acid with hydrogen. Later patents on a process involving treatment of fatty acids and their glycerides with hydrogen in the presence of catalyzers and chemically acting rays have been taken out in Austria.[232]

Utesher [233] also outlines a process for the hydrogenation of the unsaturated fatty acids or their glycerides, using the silent electric discharge. He states that care was taken that the "induction spark" was prevented from coming into contact with the fatty substances, and that only the chemically acting rays of the discharge were utilized; for example, those from a mercury quartz lamp. Utesher also obtained positive results by letting the silent electric discharge act on a catalyzer, thus not only assisting it in maintaining its activity, but in actually increasing its effect. The apparent activation of the catalyzer may be explained by the ionization of the hydrogen brought about by photo-electric forces.

Utesher,[234] in a German patent, claims a process for transforming the saturated fatty acids and their glycerides into saturated compounds by means of hydrogen. The fatty substances in the presence of hydrogen are subjected to the simultaneous action of a metallic catalyzer and the silent electric discharge.

Gruer,[235] subjected fats and oils to the action of an electric current of high potential,[236] and claims a greater effect for both current and catalytic substance when combined than for either when used separately. In this connection it is of interest to point out the observation of Farmer and Parker [237] that ultraviolet light exerts a retarding effect on the catalytic action of colloidal platinum used for breaking down hydrogen peroxide.

Ellis,[238] in commenting on the work of Farmer and Parker, says that it would appear that exposure to ultraviolet light may be expected to modify the rate of reaction in the hardening of oils. In a footnote he states that preliminary experiments point to a reduction in the iodine number of cotton-seed oil when exposed to ultraviolet light in an atmosphere of hydrogen.

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[232] *Seifen Ztg.*, 1298 (1913).
[233] "Cem. Rev. Fett.," Hertz, *Ind.*, 305 (1913).
[234] German Patent 266,662, February 18, 1912.
[235] French Patent 453,664, January 27, 1913.
[236] 50,000 to 100,000 volts.
[237] *J. Am. Chem. Soc.*, 1524 (1913).
[238] "Hydrogenation of Oils," p. 34.

Walter [239] proposed a method for the hydrogenation of oils in thin films in which he used a catalyzer, and mentioned that the operation might be carried out with the aid of chemically acting light. A patent by Walter [240] has to do with the acceleration of chemical reaction between liquids and gases by means of a contact substance or chemically acting rays.

Fuchs [241] calls attention to several theoretical considerations which if followed would facilitate the reduction of fatty bodies by hydrogen. He found that the velocity of the reaction was increased if the oil to be treated be held at a moderate temperature (0° to 150°), while the hydrogen employed is raised to higher temperature (200° to 250°). Maintaining the oil at low temperature is said to increase the quality of the final product, while the preheating of the hydrogen appears to increase the activity of the gas. Referring to the analogy between the action of heat and ultraviolet light, the above observation might furnish grounds for concluding that light might supply the necessary energy for accelerating this reaction.

Fuchs believes that it is necessary for the hydrogen to be in the atomic state before it is capable of acting on the fatty mineral. This production of the atomic state, he states, can be brought about through the application of chemically active rays. It also appears that the hydrogen molecule is dissociated when molecular hydrogen is pased over a catalyzing agent, such as platinum black or freshly prepared nickel powder, and then is allowed to diffuse under high pressure over heated plates of metal. This phenomenon would be evidence for believing that the hydrogen was ionized. Reference is made to experimental work, but no details are given in which light is employed as an aid to the reaction.

EXPERIMENTAL.

Chlorination of Acetic Acid.

An attempt was made to prepare a substitution product of acetic acid by the action of chlorine on acetic acid in the presence of artificial light.

The essentials of the method used were as follows: Chlorine, generated by the action of hydrochloric acid on potassium per-

[239] *Seifen Ztg.*, 442 (1913).

[240] German Patent 257,825, July 27, 1914; fr. Ellis, "Hydrogenation of Oils, p. 36.

[241] *Seifen Ztg.*, 40, 982–983 (1903); Belgian Patent 256,574 V–15V (1913).

manganate, was first washed with water, then with concentrated sulphuric acid, and finally passed into a quartz flask containing glacial acetic acid. The flask, fitted with a reflux condenser, was heated on a steam bath and exposed to the source of illumination. It was found that under the influence of the rays from an iron arc, placed three centimetres from the flask, monochloracetic acid was obtained, the yield being greater if red phosphorus was used as a catalyzer. Under the influence of the rays from a projection lantern about five centimetres from a glass flask, the other conditions being the same as in the previous conditions, no substitution product of acetic acid was obtained. While the negative results may have been due to the lack of intensity of the light of active wave-length and its rather limited space of action, it is probable, also, that the most active rays were excluded by the glass.

An attempt was made to prepare chloracetic acid by the action of chlorine activated by the use of ultraviolet rays. Chlorine, generated by the action of hydrochloric acid on manganese dioxide, was first purified with water and sulphuric acid, and then led through a quartz tube, 6 millimetres in diameter and about 75 centimetres long, into the flask containing glacial acetic acid. With the fact in mind that when any substance phosphoresces by the action of light it gives off charged particles of electricity capable of causing ionization in certain gases; the tube was placed on a bed of powdered fluorite. A quartz mercury lamp which operated in a 110-volt circuit was used as a source of illumination. The potential across the arc was about 80 volts. The lamp was placed above and close to the tube, so as to get a maximum effect of the waves of shortest length produced. The results of this investigation were negative.

Chlorination of Benzene and Toluene.

Experiments were performed to obtain chlorine substitution products of benzene and toluene, which paralleled in all cases those above mentioned, except with regard to temperature conditions.

At room temperatures and without catalyzers these substitution products were not obtained under the influence of the light from a projection lantern, but they could be obtained at room temperatures under the influence of the rays from an iron arc.

While an effort to obtain a substitution product of benzene using chlorine, activated by the rays emanating from a quartz mercury arc, gave (as with acetic acid) negative results, chlorination products of toluene could be obtained under similar conditions.

An endeavor was then made to chlorinate benzene and toluene at room temperatures by activating the chlorine through the agency of an electric discharge. The chlorine, generated by the action of hydrochloric acid on potassium permanganate, was purified and then led through a Siemens ozonizer into a wash-bottle which contained the benzene or toluene and was protected from the light by black paper and cardboard. The ozonizer was connected with the secondary terminals of a small induction coil capable of producing a three-centimetre spark. The results were negative.

Trinitrotoluene.

As stated above, the melting-point is of great importance in grading trinitrotoluene. The following experiments were conducted to see what effect light would have in lowering the melting-point of trinitrotoluene. The product used was one obtained from Professor Munroe, of the George Washington University.

Each sample on which observations were to be made was placed in a small "melting-point tube" made as described in Gattermann's "Practical Methods of Organic Chemistry."[242] A small cotton plug was placed in the top of the tube, and the opening was then closed with soft wax.

It was found during this work that trinitrotoluene was decomposed by sunlight, as evidenced by a darkening of the cotton plugs in the tubes, as well as by a decided lowering of the melting-point, which changed from 80.47° to 80.18° after exposure for one day, to 79.27° after exposure for one week, to 78.37° after exposure for two weeks and 77.50° after four weeks. After two hours' exposure a slight color change, but no apparent change in melting-point, was developed. It was noted, also, that the melting-point was less sharp after exposure to light, and that where decided coloring was evidenced examination under a microscope showed two sets of crystals, one set being a much darker brown, although the form was the same.

[242] Page 66 (1909).

A sample of trinitrotoluene was placed in a capillary tube made of quartz. This tube was kept in the path of the rays emanating from an iron arc (see above), which was placed 1.5 centimetres from the tube. After six hours' exposure the product was examined. It had turned a dark brown and had a melting-point of 79.06°.

Samples of trinitrotoluene, melting-point 80.47°, were placed, one in a capillary tube made of quartz, and another in a capillary tube made of glass. These tubes, together, were placed on a table 7 centimetres from a mercury quartz lamp. The heating effect of the lamp on the tubes was greatly reduced by employing a mechanical blower, so arranged as to drive a constant stream of air over the tubes. The temperature indicated by the thermometer was 30° at the beginning and 40° at the end of a three-hour period. After an exposure of the above duration the samples were examined. There appeared to be no darkening of the crystals in either tube. The melting-point of both specimens was found to be the same, namely, 80.21°.

In view of the previous experiment, this identity in the change of melting-point in samples contained in glass and quartz, and exposed to the rays from a mercury quartz light, seemed surprising. This experiment, however, indicates that artificial light materially affects trinitrotoluene, and that the long ultra-violet rays (*i.e.*, those which can pass through 7 centimetres of air) have little, if any, greater effect than the "visible" rays from a mercury quartz arc.

An experiment was performed to study the effect of sunlight on trinitrotoluene in the absence of air. It was thought that, inasmuch as the evolution of gases indicates, in general, chemical change, the use of an apparatus which would detect any such evolution would prove of value in the demonstration of the decomposition of the substance under examination. Some of the product was therefore placed in a "fermentation tube" of the type commonly used by bacteriologists in detecting gas formation by bacteria. The air in the tube was displaced by mercury. The crystals did not rise to the top of the tube, as was expected, but clung to the sides. The tubes were placed on the window-sill of a south window and allowed to remain three weeks. Observations were made every day, but there was no immediate change. As time passed, however, the product grew darker gradually, though much more slowly than in those cases when

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air was present. There also appeared to be a slight evolution of gas, which remained in contact with the crystals. The amount was too small, however, to admit of identification. It was also noted that the part of the sample which was on the side of the tube not exposed to the direct sunlight showed very little change.

The above experiments not only confirm the observations of Molinari and Quartieri,[243] but establish the fact that the ultraviolet rays are more active in producing decomposition of trinitrotoluene than rays of longer wave-length. They further indicate that the change in trinitrotoluene when exposed to light is due to oxidation.

Nicotine and Pyridine.

A study of the effects of light on nicotine and pyridine solutions, both dilute and concentrated, shows:

That there is a change in nicotine content when nicotine solutions are exposed to sunlight.

That this change is more marked in the presence of air—a fact which indicates an oxidation process.

That ultraviolet light produces a change in the nicotine in nicotine solutions.

That sunlight produces a change in pyridine in pyridine solutions.

The experiments with nicotine solutions were made on 0.1 per cent. solutions and 40 per cent. solutions which were exposed to sunlight; some in clear glass vessels and some in amber glass containers; some in the presence of air and others in which air was excluded.

It was thought that the alkalinity of such solutions might affect their change on exposure to light, so that another set of experiments was tried, using a 10 per cent. solution made acid with sulphuric acid.

The results were similar to those obtained in the unneutralized solutions. It was noted, however, that in the absence of air it made no decided difference whether the samples were exposed to light or kept in the dark, except in the case where an amber container was used, in which case there appears to be an increase in the amount of nicotine. This latter is inconsistent with the previous experiments and no explanations are offered. It, however, adds to the strength of the belief that light does effect

[243] *Loc. cit.*

a change in the nicotine, this power of causing deterioration, however, being limited to light of short wave-lengths.

A decided change in color of the solutions was also noted. The colors were compared with standard nesslerized ammonia solutions similar to those used to determine the amount of ammonia in water.

Two experiments were tried with nicotine solutions exposed in quartz flasks to ultraviolet light.

A portion of a 0.1 per cent. solution was put in a quartz Erlenmeyer flask five centimetres from an interrupted spark driven by a high-frequency current for fifteen minutes. A slight but decided decrease in the amount of nicotine was found.

A sample of a 40 per cent. nicotine solution (commercial) in a small quartz Erlenmeyer flask was placed five centimetres from an iron arc for thirty minutes. The sample, when analyzed after the exposure to the light, showed a slight but decided increase in the amount of nicotine present.

As facilities for repeating these last two experiments were not available, little value can be attached to them. The former indicates a decrease in the amount of nicotine—a fact contradicted by the results of the latter, in which the conditions were similar, but not identical. It is to be noted that the latter was carried out with a commercial sample which contained oils; and in view of the work of Inghilleri, and Paterno and Maselli, before mentioned, who reported a synthesis of alkaloids by action of light, an hypothesis to account for the apparent increase in nicotine by a synthesis of an alkaloidal substance from such oils, or even some change in the nicotine itself, is not untenable.

Since the basic properties of nicotine are attributed to the pyridine ring, it was thought interesting to undertake an experiment to show whether light had any noticeable action on pyridine. With this end in view, experiments were carried out, which correspond in their essential particulars to those reported above, using pyridine and pyridine solutions instead of nicotine, and it was found that sunlight produces a change in pyridine solutions.

The changes in pyridine were indicated by the results of quantitative analysis by the method by K. E. Schulze.[244]

[244] *Berichte*, **20**, 3391 (1887). See Treadwell, F. P., and Hall, William F., "Analytical Chemistry," vol. 2, p. 447.

Calcium Carbide and Nitrogen.

An attempt was made to determine whether there was any action between calcium carbide and nitrogen under the influence of ultraviolet light. The calcium carbide was placed in a quartz container, the supernatant air being replaced by nitrogen. The source of light was an iron arc backed by a nickel reflector. There was no apparent reaction, as a manometer connected with the cell showed no change in pressure when the temperature conditions were taken into consideration, and a test for ammonia on treating the product with hot water gave negative results.

Hydrogenation of Oleic Acid.

Experiments were performed to ascertain if there would be an acceleration of the hydrogenation of oleic acid under the influence of the rays from an iron arc. The hydrogen, generated in a Kipp apparatus by the action of hydrochloric acid on zinc, was purified by washing with lead acetate and with sulphuric acid and led into a quartz flask which contained the oleic acid. A long air condenser was passed through the stopper with which the flask was supplied. An iron arc was placed 1.5 centimetres from the flask, and exposure was allowed to proceed for six hours. The iodine numbers of the acid before and after treatment were determined with the following results:

That there is no acceleration in the hydrogenation of oleic acid when hydrogen acts on the acid in the presence of rays from an iron arc under ordinary conditions of temperature and pressure, as blank experiments have shown an amount of saturation equivalent to that found in this trial.

In consideration of repeated references to the ionization of hydrogen gas it is to be noted that hydrogen is found to occur in the following forms: H, H_2, $H+$, $H-$, H_2+;[245] neutral atomic hydrogen, neutral molecular hydrogen, atomic hydrogen bearing a positive charge, atomic hydrogen bearing a negative charge, and molecular hydrogen bearing a positive charge.

As McClung [246] and Thompson [247] have shown that a charged gas can be carried along a tube some distance before it loses its

[245] Thompson, *loc. cit.*

[246] "Conduction of Electricity through Gases and Radio-activity."

[247] "Conduction of Electricity through Gases."

charge, it was throught that an attempt to hydrogenate oleic acid by means of hydrogen made active by a silent electric discharge before being passed into the acid might yield evidence of value in proving the presence or absence of actively charged hydrogen.

The hydrogen generated as in the previous experiments was led through a Siemens ozonizer before it was passed into the oleic acid, which was held in a large test-tube. This tube was immersed in a calcium chloride bath. The temperatures selected for tests were, 20°, 125°, and 200°.

In some of the tests the ozonizer was operated by an induction coil capable of producing a three-centimetre spark, while in others a coil capable of producing a five-centimetre spark was used.

The experiments showed:

1. That oleic acid may be partially saturated by passing in hydrogen at approximately atmospheric pressure at ordinary temperatures;

2. That the action may be increased by heat; and

3. That it cannot be accelerated by activating the hydrogen by passing it through ozonizers under the conditions here mentioned.

SUGGESTIONS.

The observations made above, and experiments reported, are to be considered as preliminary only. Few as they are, they open an almost inexhaustible field for research. If attention is confined to the formation of chloracetic acid alone, which is commercially important because it takes part in the formation of indigo by one of the most successful manufacturing processes, one has only to reflect on the question of possible difference in behavior of chlorine from different sources,[248] and the different catalyzers and quantity and quality of illumination, and it may be added that chlorine itself is used as a catalyzer,[249] without considering conditions of temperature and pressure, to see that much more may be done.

[248] Cf. Russ, *loc. cit.;* Schluederberg, *J. Phys. Chem.*, 12, 574–631 (1908); Fabinyi-Klausenburg, *Ion.*, 1, 70–71; *Z. Ech.*, 503 (1902); Ludlam, *loc. cit.;* Baskerville and Riederer, *loc. cit.*

[249] Weigert, *Z. Elecktrochem.*, 14, 591 (1908); Burgess and Chapman, *loc. cit.*

It would be interesting also to try variations of the above experiments on acetic acid, benzene, and toluene, where the acetic acid, benzene, or toluene is in the vapor phase.

Furthermore, it would be interesting to conduct experiments on the activation of gases under conditions where the intensity of electric energy or light energy, as well as the distance the gas passes after activation, could be varied.

It is probable that valuable results would be obtained in many cases where attempts are made to use light as a source of energy in accelerating a chemical reaction if particular attention were paid to the absorption spectra of the reacting substances, and it is not unlikely that investigations of the effects of light present under the manufacturing conditions existing, where explosives are prepared and handled, may prove of value.

GENERAL SUMMARY.

In this work evidence is brought forth to show, first, that the well-established belief that certain chemical reactions are accelerated by light is justified, and that such effects are more marked in the presence of ultraviolet light than in the presence of light of shorter wave-length; secondly, the previously scattered evidence has been collected relative to the hypothesis that radiant heat, light, and electricity are similar from a purely physical standpoint and that they produce similar chemical changes, and additional evidence has been obtained.

By studying the effect of light on the reactions taking place between chlorine and acetic acid it was found:

1. That monochloracetic acid could be obtained under the influence of rays from an iron arc at the temperature of the steam bath when no catalyzer is used.

2. That a greater quantity of chloracetic acid could be obtained under the influence of the rays from an iron arc at the temperature of the steam bath if red phosphorus was used as a catalyzer than when no catalyzer was used.

3. That chloracetic acid, chlorination products of benzene and of toluene could not be obtained under the influence of the rays from a projection lantern.

4. That chloracetic acid and chlorination products of benzene could not be obtained from chlorine activated by the use of the rays emanating from a quartz mercury arc before passing into

acetic acid or into benzene, but that chlorination products of toluene could be obtained under similar conditions.

5. That chlorination products of benzene and of toluene could be obtained at room temperatures under the influence of the rays from an iron arc.

6. That chlorination products of benzene and of toluene could not be obtained from chlorine which was led through a Siemens ozonizer before being passed into benzene.

By a study of the effects of light on trinitrotoluene it was found:

1. That trinitrotoluene was decomposed by sunlight.

2. That ultraviolet rays are more active in decomposing trinitrotoluene than rays of longer wave-length.

3. That the change produced when trinitrotoluene is exposed to light is due to oxidation.

An unsuccessful attempt was made to form a chemical compound from nitrogen and calcium carbide under the influence of ultraviolet light.

By studying the effects of light on nicotine solutions it was found:

1. That there is a change in nicotine content when nicotine solutions are exposed to sunlight.

2. That this change is more marked in the presence of air—a fact which indicates an oxidation process.

3. That this power of causing the change is limited to light of short wave-lengths.

4. That ultraviolet light produces a change in the nicotine in nicotine solutions.

5. That sunlight produces a change in the pyridine in pyridine solutions.

6. That the alkalinity of nicotine solutions does not affect the reactions due to light.

By a study of the effect of ultraviolet light on the reaction taking place between oleic acid and hydrogen under the influence of light it was found:

1. That oleic acid may be partially saturated by passing in hydrogen at approximately atmospheric pressure at ordinary temperatures;

2. That the action may be increased by heat; and

3. That it cannot be accelerated by activating the hydrogen by passing it through ozonizers under the conditions here mentioned.

Attention is called to the fact that, from a consideration of the results obtained in experiments where attempts were made to activate gases before their contact with the liquids under consideration, it may be inferred either that ionization of the gas was not obtained or that ionization is not the condition essential for promoting the change.

It is with the greatest pleasure that I express my appreciation of the advice and encouragement received from Prof. Charles E. Munroe and Prof. N. Monroe Hopkins during the course of this work.

Laboratories of the George Washington University,
May 26, 1917.

Heating Buildings with Sprinkler Systems. E. D. DENSMORE. (*Quarterly of the National Fire Protection Association*, vol. xi, No. 2, p. 168, October, 1917.)—The increasing use of automatic sprinklers in modern commercial industrial buildings has led to the development of the sprinkler system for heating purposes. As is well known, the sprinkler system consists in general of a series of pipes which cover uniformly the ceilings of all floors. If the water which is maintained in the system can be heated and circulated, evidently the sprinkler piping can be used for heating. One fundamental objection is that the sprinkler head which is in ordinary use will melt at the temperature necessary for the water to be used for heating purposes. This melting of the sprinkler head is prevented by means of a U-connection through which the hot water cannot circulate. In practice it has been found that a bend in the horizontal nipple carrying at the end the upright sprinkler head will prevent the head from melting.

The connections of the hot-water heating system with the sprinkler piping are exceedingly simple and need not change the sprinkler piping in any way. The hot-water heater may be located in any convenient place. From the hot-water heater a hot-water supply pipe is run and connected to the foot of the sprinkler riser inside the sprinkler alarm valve. It is advisable to provide an ordinary stop valve at this point so that the hot-water supply may be entirely shut off from the sprinklers when necessary. Between the hot-water connection to the riser and the sprinkler heads no changes are made, the riser, laterals, and distributing pipes being installed in the usual way. Many successful installations have been made, and apparently no fundamental difficulties have been encountered over a period of several years in operation.

THE METALLURGY OF TITANIUM.*

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7. TITANIUM IN THE METALLURGY OF IRON.

General Statement.—The effect of titanium on cast iron has been the subject of much discussion; not a great amount of data is available for the accurate solution of the question, but the probabilities are that the action of the metal has quite contradictory effects. This is presumed to arise from its varying action with the different metalloids. In an extensive paper in 1912 before the American Institute of Mining Engineers, Bradley Stoughton recorded data pertinent to the effect of titanium on the strength of cast iron. One particular point is to be noted from his findings, for the reason that it stands forth very prominently, and that is that titanium unquestionably reduces the chill. This should not be unexpected from what is known of the action of the metal—it being one of the strongest deoxidizers known, and it further has a high chemical affinity for both sulphur and nitrogen. The question logically arises: Why does titanium reduce chill? This is readily answered. The elements oxygen and sulphur (and nitrogen, probably) are productive of chill, and titanium, by removing them, consequently removes their chill action. This shows how the chill is modified and, further, why the strength of castings is lower. The titanium not only removes the sulphur but also the oxygen.[79] The effect of titanium in reducing chill in cast iron is overcome by the use of an increased proportion of manganese for purposes of restoration—and this is decidedly met with disapproval. It appears, on the whole, that not much

* Concluded from page 650, vol. 184, November issue.

[79] The effect of small amounts of oxygen in cast iron is to increase its strength and resistance to shock. Oxygen to the amount of but 0.06 per cent. gives cast iron a tensile strength of 3500 pounds per square inch, as compared with 2500 pounds per square inch for otherwise similar non-oxygenated iron. Note Johnson, W. McA., "A Chemical Explanation of the Effect of Oxygen in Strengthening Cast Iron," *Bull. A. I. M. E.*, February, 1916, pp. 233–235.

benefit can arise from using titanium in the metallurgy of cast iron, but recently its use has been recommended by Doctor Moldenke, the American foundry expert, as worthy of employment for the removal of nitrogen and oxygen where special cast irons are to be produced. Some metallurgists held for a long time that titanium rendered cast iron tough—probably, for one reason, because the well-known pig iron of Upper Styria contains a small percentage of the metal. However, steel made therefrom rarely showed any titanium content on analysis, because of the strong affinity of the element for oxygen.

How Titanium is Used in Iron Metallurgy.—In iron foundry practice, the usual method of employing titanium is to scatter a predetermined amount of a titanium alloy (ferro-titanium or ferro-carbon titanium, as the case may be) along the runner prior to tapping. Upon tapping the cupola, the titanium alloy is washed into the ladle with the stream of iron. As in steel practice, time should be allowed for the chemical reactions to complete themselves, so that the ladle should be held for about three minutes before pouring. Also, as in steel practice, care should be taken so that the slag be not allowed to come in contact with the alloy, as slag attacks the alloy with very great avidity, thus destroying its function. Iron may also be treated in the ladle by adding the titanium alloy to the ladle either before or during tapping. In small hand ladles it is an easy matter to stir the iron with a rod in order to thoroughly incorporate the alloy into the molten bath. For usual deoxidizing purposes, about two to four pounds of a 15-per cent. titanium alloy per ton of iron will be requisite and sufficient.

Effect of Titanium Additions to Iron.—L. Treuheit [80] experimented with the effect of additions of 10 to 15 per cent. titanium and 25 per cent. titanium alloys on iron and arrives at the conclusion that the benefits derived from their use are small. The benefits usually claimed as resulting from titanium treatment of cast iron are summed up as follows:

1. An improvement in machining qualities of the iron;
2. An increase in the hardness of chill;
3. An increase in soundness of castings;
4. An increase in the strength; and
5. That but extremely small amounts of titanium are needed to produce the results given in 1; 0.04–0.05 per cent. titanium being claimed to be effective.

[80] Treuheit, L., *Stahl und Eisen*, vol. xxx, pp. 1192–1201.

Evidently the first two cannot occur together in the same iron,[81] and the variation in cast-iron samples from the same melt is often so great that it is difficult to say when improvements have really followed the titanium treatment. The chief, and seemingly the only, value of titanium in the treatment of iron lies in its ability to deoxidize the metal. The metal undoubtedly scavenges from the product of the cupola or the air-furnace oxides and occluded gases, as well as nitrides. On this basis, a certain given amount of titanium will cleanse any given iron; any less will be insufficient, while any more will not make the iron better. Sufficient titanium should be added to effect a complete deoxidation and denitrogenation of the metal. However, it is a waste of money to treat a sound metal, as no improvement can be gained in this case unless the composition of the metal is altered. Large iron castings treated with carbon-free ferro-titanium are illustrated in Figs. 22 and 23.

Titanium in the Blast Furnace.—This subject has been dealt with at some length in previous paragraphs. Suffice it to indicate here that titanium may be present to the extent of about one per cent. when the burden is titaniferous, but the element is not known to exert any particular influence on the quality of the iron. When such metal is converted into steel, the titanium is completely eliminated.

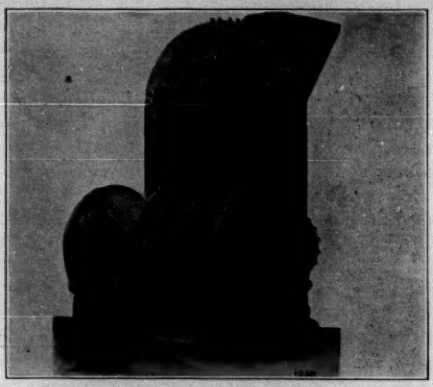
Titanium in the Foundry.—Moldenke has set forth the results of his experiments made to show the influence of titanium upon cast iron in his paper of 1908 before the American Foundrymen's Association.[82] Two series of irons were made, white and gray, and the results of his work are tabulated for brevity in Table V, page 889.

Casual examination of these results indicates that there was a distinct advantage obtained by the addition of a certain small percentage of titanium, in the case of the gray iron, but that larger additions did not result in any additional benefit. Regarding the white irons, a small advantage appears to have been secured. The above worker insists that the titanium addition is

[81] "The claim made that titanium reduces the amount of chill and at the same time makes a harder chill is preposterous" (private communication, J. E. Johnson, Jr., May 15, 1917).

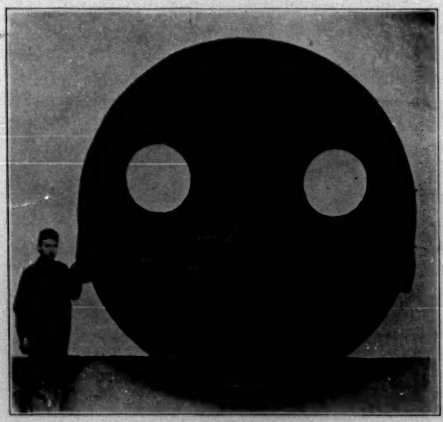
[82] Moldenke, R., "Titanium in Cast Iron," *Trans. A. F. A.*, 1908, vol. 17, pp. 57–64.

FIG. 22.



Large cast-iron cylinder head weighing 13,370 pounds treated with carbon free ferro-titanium. (After Goldschmit Thermidt Company.)

FIG. 23.



ron casting weighing 22,700 pounds treated with carbon-free ferro-titanium. (After Goldschmidt Thermit Company.)

of advantage if no more is used than is required for the purpose of deoxidation.

TABLE V.

Iron used	Per cent. titanium added	If carbon added	Broke at pounds	Deflection
Gray machinery	None	No	2020	0.09
Gray machinery	0.05	No	3100	0.09
Gray machinery	0.05	Yes	3070	0.10
Gray machinery	0.10	No	3030	0.09
Gray machinery	0.10	Yes	2990	0.095
Gray machinery	0.15	Yes	3190	0.100
White iron	None	No	2050	0.05
White iron	0.05	No	2400	0.05
White iron	0.05	Yes	2420	0.05
White iron	0.10	Yes	2400	0.05
White iron	0.15	Yes	2520	0.06

Titanium in Gray Iron.—Gray cast-iron castings normally contain about 2 per cent. or more graphite and less than 1.5 per cent. combined carbon, while the total amount of impurities present will usually be: Silicon, 0.75 to 3 per cent.; manganese, 0.30 to 0.70; phosphorus, 0.5 to 1.5, and sulphur, up to 0.20 per cent. The effect of titanium is to reduce the oxygen, nitrogen, oxides, and nitrides commonly present, and to eliminate blowholes, thereby tending towards the production of sound metal.

Titanium in Malleable Cast Iron.[83]—As is well known, malleable cast iron is produced, as indicated in the footnote, from white cast iron by either the "black-heart" or the "white-heart" process. Silicon must be low in the original iron in order that the carbon may be in the combined form as cementite. Titanium acts in a manner analogous to that of silicon; viz., it will throw down graphite and prevent the formation of Fe_3C. However this may be, the titanium will be oxidized, so that if used in small amounts its beneficial cleansing action will be secured without its entering the metal. The use of titanium alloys in the production of white

[83] Malleable castings are cast as brittle white cast iron and then made malleable by the conversion of most of the combined carbon from Fe_3C into graphite, or by oxidizing the combined carbon, or by both. The illegitimate term "semi-steel" is an indefinite trade name used at times for malleable castings. The term "semi-steel" has no meaning and should not be recognized as having any significance.

cast iron for conversion into malleable castings is as yet in the experimental stage, and no data are available.

Effect of Titanium on Chill.—The effect of titanium on chill has been indicated in the experiments of Moldenke made at the Keystone Car Wheel Works, Homestead, Pa. An iron which gave a depth of chill of 1.5 inches, not treated by titanium, showed but one inch in depth of chill when treated. Tests of the chilled part gave the results in Table VI.

TABLE VI.

Chilled iron	Pounds per square inch compression	Hardness
Treated	298,000	557
Untreated	173,000	445

An addition [84] of a one per cent. titanium alloy to a chilled iron car wheel made the metal closer grained and freer from blowholes, as well as stronger in the flanges and rims.

Effect of Titanium on the Magnetic Properties of Iron.—K. P. Applegate [85] has ascertained the effect of titanium on the magnetic properties of iron. Pure Swedish charcoal iron was treated by a 15 per cent. titanium alloy supplied by The Titanium Alloys Manufacturing Company, and with a 20 per cent. titanium alloy containing some aluminum supplied by the Goldschmidt Thermit Company. The iron-titanium alloys so secured were subjected to hysteresis tests for comparison, and these conclusions were drawn:

1. Small amounts of pure titanium (less than one per cent.) decrease to a slight extent the hysteresis losses in pure Swedish charcoal iron.
2. An increase in the percentage of titanium causes an increase in the hysteresis loss.
3. Alloys of titanium and iron are not rendered appreciably softer by prolonged annealing at 760° C.
4. The commercial titanium alloys, when dissolved in iron, yielded a metal much poorer in magnetic quality than the alloys containing pure titanium.

[84] Slocum, C. V., in a paper before the Railway Club of Pittsburgh, *Iron Age*, vol. 83, 1909, p. 1347.

[85] Applegate, K. P., "The Effect of Titanium on the Magnetic Properties of Iron," Rensselaer Polytechnic Institute, Eng. and Sci. Ser. No. 5.

5. Titanium steels are not as good as the present standard silicon steels.
6. Small amounts of pure titanium increase the permeability of pure Swedish charcoal iron.
7. The maximum induction of alloys containing titanium was considerably higher than the XI* steel or pure iron samples.
8. The permeability of the titanium specimens was higher, for the same value of H, than the XI* steel or pure iron.
9. The small percentages of pure titanium gave the lowest values for the hysteretic constant when the titanium alloys were considered. These values were, however, not as low as the hysteretic constant for the XI* steel.

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* NOTE.—The XI steel is the trade name for a steel containing from 3.5 to 4.5 per cent. silicon, used by the General Electric Company.

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CLEVELAND, OHIO,
June 9, 1917.

THEORY AND OPERATION OF DR. ZAHM'S PROPELLER COMPUTER.

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Theory.—In designing an aerial propeller by Drzewiecki's method, the blade section is assumed to act like an ordinary aerofoil, and its aerodynamical properties are assumed unchanged, due to the presence of neighboring blade sections. If we lay off along *oa*, in the following figure, the peripheral velocity of a propeller, and along *ab* the velocity of advance, then the hypothenuse *ob* will represent the resultant velocity, and *i* will be the angle of incidence, *A* the helix angle for the path of the indicated blade section.

Then the unit thrust T will be given by the equation:

$$T = L \cos A - D \sin A$$

where L and D denote the unit lift and drift of the aerofoil. But from wind-tunnel experiments we know:

$$L = K_y S V^2$$

and

$$D = K_x S V^2$$

where K_y = lift coefficient

K_x = drift

and

V = resultant velocity along the helical path in this case

S = area of aerofoil

If we call T_1 the thrust per unit area, we have:

$$T_1 = K_y V^2 \cos A - K_x V^2 \sin A$$

$$T_1 = K_y V \left(V \cos A - \frac{K_x}{K_y} V \sin A\right)$$

If we construct upon *ob* a right triangle *obe* similar to the triangle *o'b'e'* and project *oe* upon *oa*, we have:

$$og = ob \cos A - be \sin A$$

But since

$$ob = V$$

and

$$be = ob \tan \left(\tan^{-1} \frac{K_x}{K_y}\right)$$

or

$$= V \frac{K_x}{K_y}.$$

Therefore $$og = V \cos A - \frac{K_x}{K_y} V \sin A$$

Og is then equal to the expression included in the parenthesis in the thrust equation, and is called the thrust factor, and the equation then becomes:

$$T_1 = K_y V \times og$$

The efficiency of a blade section is expressed by the well-known formula:

$$\text{Efficiency} = \frac{\tan A}{\tan (A + G)}$$

where

$$G = \text{gliding angle} = \frac{K_x}{K_y}$$

or

$$\text{Efficiency} = \frac{hg}{og} \div \frac{ge}{og} = \frac{hg}{ge}$$

Construction of the Computer.—The theory upon which the computer is based has been delineated above, and it remains to be put in the form of a chart for practical use.

If we mark on *oy* the velocity of advance, on *ox* the peripheral velocity, both in miles per hour, and upon *ox* erect a number of ordinates having the values of R.P.M. and blade-section radii labelled upon them to correspond to the peripheral velocity shown on *ox*, the resultant velocity in miles per hour is at once indicated by the position and magnitude of *ob* for any combination of values of R.P.M. and velocity of advance. The helical angle *A* is indicated by the angle *ob* makes with *ox*, and its value in degrees is marked on the right-hand border of the chart.

In the thrust equation, if we put *V* in miles per hour, K_y and K_x in absolute units, we must multiply the equation by a constant, 0.0051, in order to have T_1 in pounds per square foot at standard atmospheric density. Then

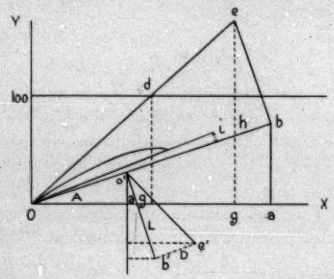
$$T_1 = 0.0051\ K_y V (V \cos A - \frac{K_x}{K_y} V \sin A)$$

To represent *ob* or *V* in the chart, a line *ob''* is scribed in a piece of celluloid having an L shape, as shown in Fig. 2, and the head of the L is pivoted at *o*, Fig. 1. On *ob''* are marked the values of 0.0051 *V*, and on *b''e''* the values of $\frac{K_x}{K_y}$ for different angles of incidence. A thread is stretched from *o* to a runner which slides on the celluloid arc *b''e''*. It represents the line *oe* in Fig. 1. A small celluloid T-square, with a black centre

line along its length, is placed perpendicular to ob'' in Fig. 2, and is used to represent be in Fig. 1.

Since the efficiency is equal to $\frac{hg}{eg}$ Fig. 1, we drop a perpendicular upon ox from d, the point of intersection of oe (or the

FIG. 1.

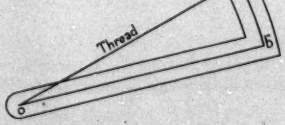


thread), with the horizontal line representing the velocity of advance at 100 miles per hour, we have then:

$$\text{Efficiency} = \frac{h\,g}{e\,g} = \frac{h^1\,g^1}{d\,g^1} = \frac{h^1\,g^1}{100} = h^1\,g^1 \text{ per cent.}$$

The vertical scale for the velocity of advance is therefore also

FIG. 2.



the scale of efficiency in per cent., and the efficiency can be read directly.

Having found the values of the thrust factor, efficiency, and 0.0051 V from the chart, the thrust per foot run of blade is:

T = blade width in feet $\times$ T_1 = 0.0051 V $\times$ K_y $\times$ thrust factor $\times$ width . . (1)

The torque L' per foot run is obviously

$$L' = c \frac{Va}{N} \frac{T}{E} \quad \ldots \ldots (2)$$

where Va is the forward velocity, E the efficiency of the blade section, N the angular velocity, and c is a constant depending upon the choice of units. If T be pounds, L pound-feet, Va miles an hour, N revolutions per minute,

$$L = 14 \frac{Va}{N} \frac{T}{E}$$

Before using the computer the aerodynamical properties of the blade sections at different radii and the blade widths must be known. The former may be found in the British Aeronautical Report, Eiffel, and other aerodynamical laboratory reports. A series of aerofoils that have been tested in the National Physical Laboratory in England, and is often used for propeller-blade sections, is found in the British Aeronautical Report, 1911–12.

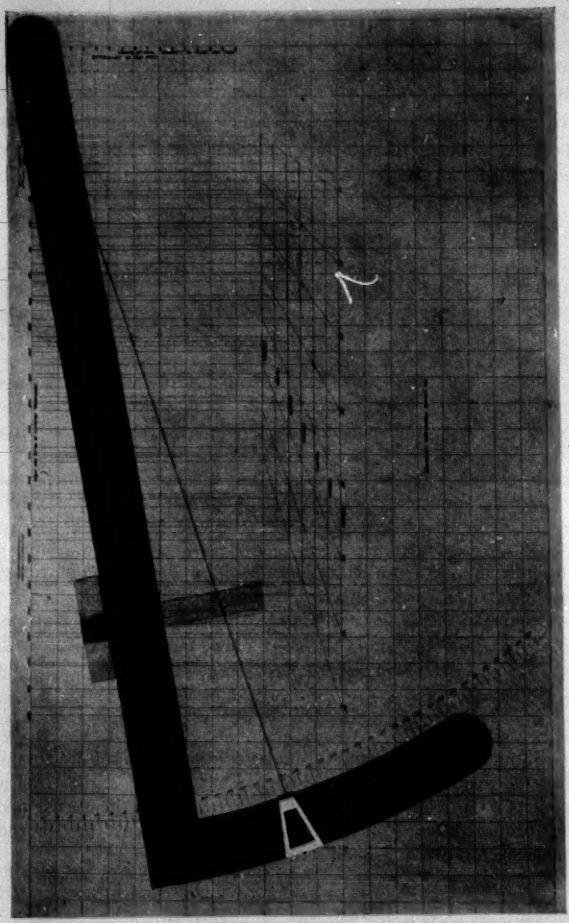
Illustration:

Let N = 1300 R.P.M.
r = 30 inches
Va = 90 M.P.H.

1	2	3	4	5	6	7	8	9	10	11	12
Section in feet	Chord length in feet	Blade axle in degrees	Angle of attack	Blade curve	Lift-coefficient	Drift lift	Section efficiency	0.005 Va	Thrust factor	Thrust per foot run	Torque per foot run
1½											
2											
2½	1.15	23.2	2	5	0.300	0.090	0.780	1.248	224	96.5	120
3											
3½											

In the above table columns 2, 3, and 5 are fixed by the designer, columns 6 and 7 are found from the British Aeronautical Report, 1911–12; columns 4, 8, 9 and 10 are found from the computer, and the last two columns are computed by equations (1) and (2).

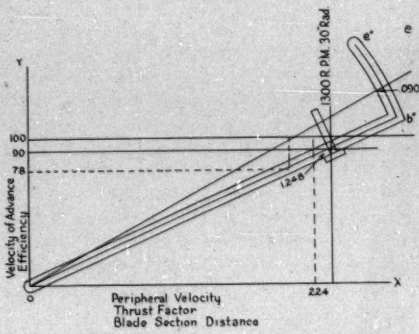
Having found the lift coefficient and $\frac{\text{drift}}{\text{lift}}$ ratio for the given blade section, firstly, swing the L piece until its line ob'' passes through the intersection of the 90-mile line and the 1300



Dr. Zahm's propeller computer.

R.P.M. 30-inch radius line and notice the reading on ob''. It is 1.248. Put this value in column 9 in the above table. Secondly, set the small T-square with its edge at the point 1.248, as shown in the diagram, and then swing the thread until it coincides with the 0.090 mark on the $\frac{\text{drift}}{\text{lift}}$ scale. The intersection of the T-square with the thread gives the thrust factor 224 as indicated on OX. From the point of intersection of the thread and the

FIG. 3.



100-mile line drop a vertical line to ob'' and read the efficiency on the vertical scale, which is 78 per cent. in this case.

Then the thrust per running foot of blade is:

$$T = \text{blade width} \times \text{lift coefficient} \times 0.005\ Va \times \text{thrust factor}$$
$$= 1.15 \times 0.300 \times 1.248 \times 244 = 96.5 \text{ pounds}$$
$$\text{Torque per running foot} = 14\,\frac{90 \times 96.5}{1300 \times .78}$$
$$= 120 \text{ foot-pounds}$$

Similarly the thrust and torque of the other sections are found. Plot the thrust, torque, and efficiency curves with radius of the sections as abscissæ. Intergate the areas under the thrust and the torque curves. Then we have the total thrust torque and efficiency for the two-blade screw:

$$\text{Total thrust H. P.} = \frac{\text{Thrust per blade} \times 2 \times \text{Va in feet per second}}{550}$$
$$\text{Total torque H. P.} = \frac{2\pi n}{33000} \times \text{torque per blade} \times 2$$
$$\text{Overall efficiency} = \text{Thrust H. P.} \div \text{Torque H. P.}$$

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

A SIMPLIFIED METHOD OF WRITING DEVELOPING FORMULÆ.[1]

By C. E. K. Mees.

[ABSTRACT.]

THE usual methods of writing developing formulæ make it very difficult to compare different formulæ, so that it is not unusual to find several formulæ which are apparently quite different, but which, if written in the same form, prove to be identical in composition.

In order to facilitate the comparison of formulæ, it is convenient to be able to write a formula in one line, thus enabling a number of formulæ to be written under one another and compared at a glance; the following notation enables this to be done.

The formulæ are expressed in grammes per litre, the water being omitted, then if R stands for the reducing agent, A the alkali, S the sulphite, and B the bromide, the formula is always written in the order R A S B, which is used as a mnemonic. Thus 5–50–50–1 means 5 grammes of reducing agent, fifty of alkali, fifty of sulphite, and one of bromide per litre.

In order to indicate the particular substances used, the reducing agents are represented by initial letters—P for pyro, H for hydrochinon, and so forth; while if no other specification is given, A represents sodium carbonate dry, S sodium sulphite dry, and B potassium bromide; thus P5–15–10–0 represents the following developer:

Pyro	5 gms.
Sodium carbonate (anhydrous)	15 gms.
Sodium sulphite (anhydrous)	10 gms.
Water to	1000 c.c.

Other chemicals are represented by their formulæ or by any other convenient abbreviation, so that the well-known hydro-

* Communicated by the Director.

[1] Communication No. 52 from the Research Laboratory of the Eastman Kodak Company, published in *British Journal of Photography*, 1917, p. 535.

chinon-caustic potash formula used for process plates may be written H12.5–KOH25–Meta25–12.5, this corresponding to:

A.	Hydrochinon	12.5 gms.
	Potassium metobisulphite	25 gms.
	Potassium bromide	12.5 gms.
	Water	500 c.c.
B.	Caustic potash	25 gms.
	Water	500 c.c.

Use equal parts *A* and *B*.

A convenient means of classifying developers containing a mixture of metol and hydrochinon as the reducing agent has been in use for some time in our Research Laboratory.

As a result of a series of measurements it was found that the formula 5–25–55–1.5 was most convenient and suitable for these developers, and this formula was entitled MQX, the suffix *X* representing the percentage of the reducing agent, which is metol; thus MQ_{20} corresponds to 20 per cent. metol, 80 per cent. hydrochinon, or a developer of the formula:

Metol	1 gm.
Hydrochinon	4 gms.
Sodium carbonate	25 gms.
Sodium sulphite	75 gms.
Potassium bromide	1.5 gms.
Water to	1000 c.c.

MQ_0 represents the same formula without metol and with 5 grammes of hydrochinon, MQ_{50} corresponds to 2½ grammes metol and 2½ grammes hydrochinon, and MQ_{100} to 5 grammes metol without hydrochinon.

The most useful members of this series have proved to be MQ_0, MQ_5, MQ_{25}, MQ_{50}, and MQ_{80}.

THE FRANKLIN INSTITUTE

OFFICERS AND MEMBERS OF COMMITTEES WHO ARE NOW IN THE ACTIVE MILITARY OR NAVAL SERVICE OF THE UNITED STATES GOVERNMENT.

Name and rank	Position	Branch of service	Location
Major R. B. Owens	Secretary	Signal Corps	France
Capt. T. F. Clark	Board of Managers	Field Artillery	Camp Meade
Mr. W. C. Wetherill	Board of Managers	Navy Aviation Dept.	Boston
Lieut. H. B. Allen	S. & A. Committee	Ordnance Dept.	France
Lieut. E. L. Clark	S. & A. Committee	Signal Corps	Camp Devens
Major G. S. Crampton	S. & A. Committee	Director of Field Hospitals	Camp Hancock
Lieut. T. R. Parrish	S. & A. Committee	Signal Corps	Washington
The following are doing special Government work:			
Mr. Charles Day	Board of Managers	Member of Commission to study shipping situation	London
Dr. T. D. Cope	S. & A. Committee	Research work	Washington
Mr. F. H. Gilpin	S. & A. Committee	Testing Department	Picatinny Arsenal

Certain definite activities have been undertaken by the Institute, as follows:

1. An office for the registration of men wishing to enter the Aviation Section of the Signal Corps was conducted during the summer by Dr. George F. Stradling, member of the Institute. Registration is still being carried on, and up to the present time 837 applications have been received and forwarded to the proper authorities.

2. Another direction in which the Institute has been of service is in the making of searches and submitting reports on various subjects to the National Research Council.

3. During the summer, at the suggestion of the Shipping Board of the United States, the President of the Institute authorized the organization of a School of Navigation. This School was carried on for several weeks at the Institute, and was then transferred to other quarters, at the University of Pennsylvania.

4. In response to a request from the Federal Board for Vocational Education, of Washington, D. C., the Institute has recently organized and is now carrying on a school for the training of men in receiving and sending wireless messages. Membership in the classes of this school is restricted to conscripted men who are sure to be included in the next or following calls, and whose physical eligibility for the service has been established.

PROCEEDINGS OF THE STATED MEETING HELD WEDNESDAY, NOVEMBER 21, 1917.

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, November 21, 1917.

PRESIDENT DR. WALTON CLARK *in the Chair.*

Additions to membership since last report, 10.

Mr. Louis E. Levy, Acting Chairman, Committee on Science and the Arts, reported the condition of the work of the committee. The Chairman announced that the first business of the meeting was the presentation of the medals recommended for award by the Committee on Science and the Arts. A telegram was read from Mr. Thomas Bilyeu, of Astoria, Ore., stating that he was occupied with war duties which would prevent him from attending the meeting, and requesting that the ceremonies in connection with the presentation of the John Scott Medal to him be postponed for one month in order that he might make arrangements to be present.

Mr. Louis E. Levy was then recognized and described the coin sorting, counting, and recording apparatus of the International Money Machine Company, to whom was awarded the Edward Longstreth Medal of Merit.

The President presented the medal and accompanying certificate to Mr. H. D. Hoffman, representative of the company. Mr. Hoffman, in accepting the award, expressed the appreciation of his company for the honour conferred upon it.

Mr. Levy was again recognized and described the Chainomatic Balance, a device for making weighings more accurately and rapidly than heretofore. He introduced Mr. Christopher A. Becker, of the firm of Christian Becker, Inc., of New York City, inventors of the Chainomatic Balance, to whom had been awarded the Edward Longstreth Medal of Merit. The medal was presented to Mr. Becker, who thanked the Institute for the recognition bestowed upon them.

M. C. Whitaker, M.Sc., D. Chem. Eng., Vice-President, U. S. Industrial Alcohol Company, New York City, N. Y., presented a communication on "Industrial Alcohol." The present state of development of the industrial alcohol industry in the United States, compared with developments in foreign countries, was discussed. Mention was made of the raw materials now used and prospects for future development of new sources of supply. The technical principles and problems involved in the manufacture of alcohol from various raw materials were described, and a forecast was made of the lines for future development, both in manufacture and in the use of the products. A comparison was made of the government regulations and restrictions which tend to develop or retard the alcohol industry in various countries. The subject was fully illustrated by lantern slides.

After a brief discussion the thanks of the meeting were extended to Doctor Whitaker for his interesting paper.

Adjourned.

GEORGE A. HOADLEY,
Acting Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of the Stated Meeting held Wednesday, November 7, 1917.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, November 7, 1917.

MR. LOUIS E. LEVY, *Chairman pro tem.*

The following reports were presented for first reading:

No. 2693.—Dressler Tunnel Kiln. Report referred back to Sub-Committee for further information.

No. 2701.—Talbot Air Lift. Report referred back to Sub-Committee for further information.

No. 2705.—Levy Hæmocytometer.

GEO. A. HOADLEY,
Acting Secretary.

SECTIONS.

Section of Physics and Chemistry.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, October 25, 1917, at 8 o'clock, with Dr. Gellert Alleman in the chair. The minutes of the previous meeting were read and approved.

David Fairchild, Sc.D., Agricultural Explorer in Charge of the Office of Foreign Seed and Plant Introduction, United States Department of Agriculture, Washington, D. C., delivered a lecture on "The Palate of Civilized Man and Its Influence on Agriculture." The influence of custom and fashion on the dietary was discussed, and a description was given of various foreign fruits and vegetables which have been introduced into the United States during the past twenty years. The lecture was illustrated with specimens and lantern slides.

The paper was discussed by Doctors Hoadley, Harshberger, C. A. Smith, and others. On motion of Mr. Louis E. Levy a vote of thanks was extended to Doctor Fairchild. The meeting then adjourned.

JOSEPH S. HEPBURN,
Secretary.

Electrical Section.—A joint meeting of the Section and the Philadelphia Section, American Institute of Electrical Engineers, was held in the Hall of the Institute on Thursday, November 1, 1917, at 8 o'clock P.M.

In the absence of the chairmen of both sections, the meeting was presided over by Doctor Carl Hering.

W. F. G. Swann, A.R.C.S., D.Sc., Chief of the Physical Division, Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, D. C., delivered a lecture on "Atmospheric Electricity."

The lecturer reviewed our present knowledge and the theory of atmospheric ionization and performed experiments showing how this ionization was increased by external causes, as by a flame and by the rays emanating from a glass tube containing radium. The radio-active materials in the soil were shown to be one of the sources for maintaining the atmospheric

ionization, and comparisons were shown of figures taken over land and over sea, the latter being obtained on one of the recent voyages of the non-magnetic ship *Carnegie* belonging to the Carnegie Institution.

The lecturer included slides of this vessel and a description of the apparatus used in making the measurements.

The evening was concluded by a brief consideration of G. C. Simpson's theory of thunderstorms.

The thanks of the meeting were extended to the speaker.

H. CALVERT,
Secretary.

Mining and Metallurgical Section.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, November 8, 1917, at 8 o'clock, with Dr. Harry F. Keller in the chair. The minutes of the previous meeting were approved as read.

Edward W. Parker, Director of the Anthracite Bureau of Information, Wilkes-Barre, Pa., late Statistician in Charge of the Division of Mineral Resources, United States Geological Survey, presented a communication on "The Problem of Coal Supply." The coal resources of the United States were described with respect to their location, extent, and character. The relation between population and coal production was pointed out. Stress was placed on the influence of the coal industry on the industrial growth of the nation. An account was given of the changes in the fuel situation which have occurred as a result of the world war. The address concluded with a series of lantern slides showing past and present-day conditions in the anthracite region.

The paper was discussed at length; a vote of thanks was extended to Mr. Parker, and his communication was referred to the Committee on Publications. The meeting then adjourned.

JOSEPH S. HEPBURN,
Acting Secretary.

Section of Physics and Chemistry.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, November 15, 1917, at 8 o'clock, with Prof. Alexander E. Outerbridge, Jr., in the chair. The minutes of the previous meeting were read and approved.

William Porter White, Ph.D., of the Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C., delivered an address on "Heat and Temperature Measurement, with Special Reference to Industrial Work." The evolution of the calorimeter was traced, and the good and bad points of each type of instrument were pointed out. The mercury thermometer, resistance thermometer, and thermocouple were described, and the advantages and disadvantages in the use of each were enumerated. The lecture was illustrated with lantern slides.

Doctors Northrup, Hering, White, Professor Outerbridge, Mr. Clamer, and others participated in the discussion. On motion of Mr. Clamer, seconded by Doctor Northrup, a vote of thanks was extended to Doctor White. The meeting then adjourned.

JOSEPH S. HEPBURN,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, November 14, 1917.)

RESIDENT.

MR. FELIX A. BOERICKE, Bryn Athyn, Pa.
DR. JOHN J. BOERICKE, Merion, Pa.
DR. EDWARD E. MARBAKER, Chemist, 224 South Fifty-ninth Street, Philadelphia, Pa.
MR. E. J. WHITE, Chemist, Ninth and Westmoreland Streets, Philadelphia, Pa.

NON-RESIDENT.

MR. G. EDWARD BARNHART, Signal Corps Aviation School, Cottage B-6, Unit No. 1, Dayton, Ohio.
MR. ENRIQUE BUSTOS, Mechanical Engineer, Baltimore Copper Works, Baltimore, Md.
CAPTAIN AUSTIN L. HODGES, Physicist, Frankford Arsenal, Bridesburg, Philadelphia, Pa.
MR. SAMUEL SPITZ, Inventor, 372 Bellevue Avenue, Oakland, Calif.
MR. JOHN F. WARWICK, Electrical Engineer, Box 3108, Boston, Mass.

ASSOCIATE.

MR. STUART D. KERR, 300 Main Street, Darby, Pa.

CHANGES OF ADDRESS.

MR. JOHN CALDER, Aeromarine Plane and Motor Company, Keyport, N. J.
MR. CLARENCE R. CLAGHORN, Vinton Colliery Company, Claghorn, Delaware County, Pa.
MAJOR A. S. CUSHMAN, 135 South Eighteenth Street, Philadelphia, Pa.
MR. FRED. DENIG, 2166 Fourteenth Street, Troy, N. Y.
MR. FREDERICK A. DOWNES, 414 Widener Building, Philadelphia, Pa.
MR. CHARLES N. FORREST, The Barber Asphalt Paving Company, Maurer, N. J.
MR. HENRY GLOVER, Fairfax Apartments, C-5, Wayne Avenue and School Lane, Germantown, Philadelphia, Pa.
MR. GEORGE R. HENDERSON, Aldine Hotel, Philadelphia, Pa.
MR. EDWIN WALKER KELLY, 312 Wisconsin Avenue, Oak Park, Ill.
MR. GEORGE H. MCFADDEN, 121 Chestnut Street, Philadelphia, Pa.
MR. C. L. MCILVAINE, 191 Hodge Avenue, Buffalo, N. Y.
MR. WILLIAM S. MURRAY, B-1017, Waterbury, Conn.
MR. LAWRENCE T. PAUL, 776 Drexel Building, Philadelphia, Pa.
COL. SAMUEL REBER, Army Building, 39 Whitehall Street, New York City, N. Y.
MR. J. J. RHOADS, 407 West Second Street, Oil City, Pa.
MR. WILLIAM H. RICHMOND, Richmond Villa, Scranton, Pa.
MR. EDWARD RITTENHOUSE, 2561 North Front Street, Philadelphia, Pa.
MR. F. R. WADLEIGH, 24 Broad Street, New York City, N. Y.

MR. SAMUEL T. WAGNER, School House Lane, Germantown, Philadelphia, Pa.
MR. NORMAN T. WHITAKER, 230 Whitaker Building, Washington, D. C.
MR. R. A. WIDDICOMBE, 5647 Kenmore Avenue, Edgewater Station, Chicago, Ill.

NECROLOGY.

Mr. R. B. Kendig, Hawthorne Avenue, Port Chester, N. Y.

Mr. George E. Bartol, Room 58, The Bourse, Philadelphia, Pa.

LIBRARY NOTES.

PURCHASES.

ALT, H. L.—Mechanical Equipment of School Buildings. 1916.
AUDSLEY, G. A. and B.—Art of Polychromatic and Decorative Turning. 1916.
CLEWELL, C. E.—Handbook of Machine Shop Electricity. 1916.
CROFT, TERRELL.—Practical Electrical Illumination. 1917.
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HARDING, L. A., and WILLARD, A. C.—Mechanical Equipment of Buildings, vol. 2. 1917.
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MARTIN, GEOFFREY.—Industrial and Manufacturing Chemistry, 2 volumes. 1917.
MILLIKAN, R. A.—The Electron. 1917.
National Association of Cement Users. Proceedings, vols. 9–10. 1912–1914.
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Royal Ontario Nickel Commission, Report and Appendix, 1917. Toronto, 1917. (From the Commission.)

S. K. F. Ball Bearing Company, Wood-working Precision at High Speed. Hartford, Conn., 1917. (From the Company.)

Second Pan-American Scientific Congress, Proceedings, vols. iv, v, vii, ix, and x, and Report of the Secretary General. Washington, 1917. (From the Congress.)

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Westinghouse Lamp Company, Increasing and Improving Production, by R. T. Kent. New York, 1917. (From the Company.)

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BOOK NOTICES.

OCEAN MAGNETIC OBSERVATIONS, 1905–1916, AND REPORTS ON SPECIAL RESEARCHES, by L. A. Bauer, Director, with the Collaboration of W. J. Peters, J. A. Fleming, J. P. Ault, and W. F. G. Swann. Washington, Carnegie Institution of Washington, 1917. 447 pages, illustrations, tables, plates, quarto. Price $10.

In this volume we have a lucid and complete account of the magnetic surveys of the ocean conducted by the Carnegie Institution on the two vessels, the *Galilee* and its successor, the *Carnegie*. The observing instruments are discussed and portrayed, the methods of observation and reduction are stated, specimen observations are given, and extensive tables present the final results. The charts of the cruises show numerous closed loops intentionally produced in order to facilitate a mathematical attack upon some of the general problems of the earth's magnetism.

It is interesting to read with what success all magnetic substances were banned in the construction of the *Carnegie* except about 600 pounds of springs, valves, etc., entirely essential to the gas producer and the internal-combustion engine. One very practical and immediately available product of the survey is the possibility of correcting the charts of magnetic declination used by mariners. In very many localities these charts are incorrect by less than two degrees. This means that a ship's master, knowing his location on the earth's

surface and having such a chart and a mariners' compass, would be able to fix a true north to south line with an error less than two degrees. Near Queen Mary's Land, southwest of Australia, however, the British and the United States charts were 12 degrees and the German charts no less than 16 degrees in error.

The volume is splendidly illustrated. The frontispiece, a picture of the *Carnegie*, is a delight to the eye. The friends of the Director will be able to recognize his face in another illustration.

It is with a feeling of pride that the volume is laid down. A great and permanent contribution has been made by American science to the world's knowledge of terrestrial magnetism, and the form of presentation is worthy of the contents.

GEORGE F. STRADLING.

NOTIONS GÉNÉRALES SUR LES APPAREILS À REACTION, par Paul Popovatz. Paris, Gauthier-Villars et Cie, 1916. 36 pages, 5½ × 9 inches, paper, 1 franc 50.

Always of the greatest interest, at the present time more than ever before, the subject of propulsion by reaction is one of the highest importance. In both marine and aerial propulsion the greatest progress has been made by the slow process of evolution from experimental data. It is true that formulas for thrust, power, efficiency, and the like have been derived in works on hydraulics and monographs on propulsion; but the problem has not yielded to theoretic treatment as readily as other hydraulic problems, and it has been the practice in important work to design propellers for marine vessels by experiments on models from which the performance of the full-size propeller may be calculated. More recently, however, there has been a disposition to analyze the problem more minutely from a theoretic point of view with the object of establishing dynamical formulas with coefficients more widely applicable than those in common use. Undoubtedly it is only on such a sound basis that a satisfactory theory of design can be established.

The present work is devoted to that end by an analysis of the principles of reaction apparatus based upon the fundamental formulas of momentum and kinetic energy. Throughout the work the deductions of the relationship of thrust, power, and efficiency are made with the greatest clarity from carefully considered premises, leaving the reader in no uncertainty as to the significance of the conclusions.

Among the features of particular interest are those relating to a rational mode of estimating efficiency and a theoretical deduction of the diameter of the jet obtained from a propeller of given diameter, a quantity previously determined only by experiment. On the question of efficiency, the author points out that most writers consider efficiency from the standpoint of the product of velocity of the vessel and thrust. This mode of rating efficiency is obviously, as he states, wholly inapplicable when the vessel is stationary or lifted by the reaction of a jet; and he lays stress on the value of considering efficiency in terms of jet-velocity for comparing the performance of vessels operating under varying conditions of motion.

This brief work is a model of logical deduction of the principles of jet reaction and should prove a material aid in placing the design of propelling apparatus on a rational basis.

LUCIEN E. PICOLET.

THE J. E. ALDRED LECTURES ON ENGINEERING PRACTICE, Department of Engineering, Johns Hopkins University. Baltimore, The Johns Hopkins Press, 1917. 246 pages, 6 × 9 inches, paper.

It has long been the custom of engineering schools to include in their curricula a number of lectures on subjects of applied engineering by engineers actively identified with professional practice, a procedure upon whose educational value it is scarcely necessary to dwell. The course maintained in the Department of Engineering of Johns Hopkins University is one feature of a general plan, made possible by the gift of Mr. J. E. Aldred, for furthering and improving undergraduate instruction in the methods and problems in the practice of engineering.

The lectures deal, therefore, with everyday working methods of design, construction, and operation rather than with underlying theory. During the year 1916–1917 three lectures each have been given on the general subjects of civil, electrical, and mechanical engineering. They cover hydraulic and steam power projects and gas manufacture; transportation; structural design; sanitation; and corporate and public utility finance. The lectures will be given in succeeding years, in accordance with the same general plan. They are given in the afternoon and are open to the public.

LUCIEN E. PICOLET.

PUBLICATIONS RECEIVED.

Lubricating Engineers' Handbook: A reference book of data, tables and general information for the use of lubricating engineers, oil salesmen, operating engineers, mill and power-plant superintendents and machinery designers, etc., by John Rome Battle (B.S. in M.E.).—333 pages, illustrations, plates. 8vo. Philadelphia and London, J. B. Lippincott Company, 1916. Price, $4.

Laboratory Guide of Industrial Chemistry, by Allen Rogers, in charge of Industrial Chemistry, Pratt Institute, Brooklyn, N. Y. Second edition, entirely rewritten and enlarged. 212 pages, illustrations, 12mo. New York, D. Van Nostrand Company, 1917. Price, $2.

El Levantamiento de la Carta Militar de la Republica Mexicana. Proyecto que presentan a la consideracion del Ciudadano Presidente de la Republica los Ingenieros General Maximiliano Klos y Teniente Coronel Francisco Diaz Babio. 63 pages, illustrations, plates, 8vo. Mexico, 1917. Price, $3.

United States Weather Bureau: Daily River Stages at River Gauge Stations on the Principal Rivers of the United States, vol. xiv for the year 1916, by Alfred J. Henry, Professor of Meteorology. 278 pages, quarto. Washington, Government Printing Office, 1917.

North Carolina Geological and Economic Survey: Economic Paper No. 44, Highway Work in North Carolina During the Calendar Year Ending December 31, 1914: A Statistical report compiled by Joseph Hyde Pratt, State geologist, and Miss H. M. Berry, secretary. 64 pages, 8vo. Economic Paper No. 45, Proceedings of Eighth Annual Drainage Convention of the North Carolina Drainage Association, held at Belhaven, N. C., November 29, 30, and December 1, 1915. Compiled by Joseph Hyde Pratt, State geologist, and Miss H. M. Berry, secretary. 90 pages, 8vo. Raleigh, State printers, 1917.

Canada Department of Mines, Mines Branch: The Production of Iron and Steel in Canada During the Calendar Year 1916, by John McLeish, B.A., Chief of the Division of Mineral Resources and Statistics. 50 pages, 8vo. Ottawa, Government Printing Bureau, 1917.

U. S. Bureau of Mines: Bulletin 136, Deterioration in the Heating Value of Coal During Storage, by Horace C. Porter and F. K. Ovitz. 38 pages, illustrations, 8vo. Bulletin 139, Control of Hookworm Infection at the Deep Gold Mines of the Mother Lode, California, by Dr. James G. Cumming, Director of the Bureau of Communicable Diseases, California State Board of Health, and Joseph H. White, Sanitary Engineer, U. S. Bureau of Mines. 52 pages, illustrations, 8vo. Monthy Statement of Coal-mine Fatalities in the United States, August, 1917. 27 pages, 8vo. Technical Paper 98, Effect of Low-temperature Oxidation on the Hydrogen in Coal and the Change in Weight of Coal on Drying, by S. H. Katz and H. C. Porter. 16 pages, illustrations, 8vo. Washington, Government Printing Office, 1917.

U. S. Department of Agriculture: Circular 79, Emergency Fuel from the Farm Woodland, by A. F. Hawes, Extension Specialist. 8 pages, 8vo. Washington, Government Printing Office, 1917.

Natural Reproduction from Seed Stored in Forest Floor, by J. V. Hofmann. Reprinted from *Journal of Agricultural Research*, vol. xi, No. 1. 26 pages, plates, map, 8vo. Washington, Government Printing Office, 1917.

U. S. Bureau of the Census: Census of Manufacturers, 1914. Agricultural implements. Prepared under the supervision of W. M. Stewart, chief statistician of manufactures. 12 pages, quarto. Washington, Government Printing Office, 1917.

Etching Steel Electrically. ANON. (*Scientific American*, vol. cxvii, No. 18, p. 334, November 3, 1917.)—An electric pencil or "etchograph" for writing or drawing on a piece of steel, so that the marking is etched deeply and permanently, has been perfected by William Brester, of New York City. The device consists of a pencil member and a step-down transformer which can be connected to an alternating-current socket. From the secondary or low-voltage side of the transformer one lead is connected to the work, the other to the pencil member. The pencil has a hard-rubber handle and a metal clamp which holds a short length of ordinary copper wire.

As the electric pencil is drawn over the steel surface of the work, great heat is developed at the point of contact. The etching depth can be readily varied by means of a rheostat. Operating on a 110-volt, 60-cycle circuit, the transformer requires a current of 1½ to 2 ampères and delivers about 20 ampères at 2 volts to the copper point of the pencil. It is said that the etchograph is adapted to marking either iron or steel, and all classes of high-speed carbon and machine steel, whether in the hardened or soft condition.

CURRENT TOPICS

Plumbago Crucibles. ANON. (*Engineering and Mining Journal*, vol. 104, No. 18, p. 797, November 3, 1917.)—The manufacture of plumbago crucibles has been seriously affected by conditions due to the present war. The disturbances have extended to the users of crucibles, involving increased costs and in some cases reducing output because of the shortage of crucibles of the proper quality.

The important and essential ingredients of plumbago crucibles are the plumbago and the clay which serves to hold the crucible together during manufacture and in use. The supply of plumbago comes largely from the Island of Ceylon. In October, 1914, the British Government placed an embargo on plumbago exports from Ceylon lasting more than four months. This exhausted the reserve stocks of American manufacturers. After the embargo was raised shipments were generally regular enough to meet requiremnets except for short periods. Before the war all the clay for plumbago crucibles was imported almost exclusively from the town of Klingenberg, in the western part of Germany. The clay is remarkably clear and uniform, and the deposit large enough to supply all demands that have been made upon it.

Soon after the war Germany prohibited the shipment of this clay, and it became necessary to find a substitute. In trying out different mixtures the plan was adopted to make trial lots of six crucibles from each blend of clay. As it takes from two to three months to make and burn crucibles and get results from tests of users, progress is slow. While before the war 25 to 30 heats were secured from each crucible, the first use of domestic clays gave only four or five. At present, however, 15, 20, and 25 heats are obtained from an average size crucible, such as No. 80, used in standard rolling-mill practice. By a process of elimination the clays now in use are comparatively few, and a steady improvement is expected in the quality of crucibles. However, the cost of the domestic clay is more than double that of the German clay.

Recent Industrial Uses of Aluminum. F. G. SHULL. (*Journal of the American Institute of Metals*, vol. xi, No. 1, June, 1917.)—Aluminum is now so widely used for a variety of purposes in different forms that new applications and new forms of the metal come into use almost unnoticed. The new forms that have acquired commercial importance only in very recent years are: aluminum foil; aluminum bottle caps and jar closures; manufactures involving antogenous welding; die and pressed castings; tubing for store service; rolled rod for machining purposes; and aluminum conductors, steel reinforced.

The aluminum foil industry has grown from practically nothing to a volume of business involving many tons of aluminum annually. Aluminum foil, printed and embossed, is extensively used as a protection and ornamental wrapper for soaps, confectionery, and the like. Plain foil is used to some extent in electrical condensers. The most recent use is for the lining of pulp-board cartons for the packaging of coffee. This combination of package possesses moisture-resisting and oil-retaining characteristics not inferior to the tin can as a coffee container.

The development of a process of welding aluminum by means of the oxyhydrogen and oxyacetylene flame has opened an almost limitless field for the outlet of aluminum. Sheet aluminum of all gauges thicker than one thirty-second of an inch can be readily welded and the seam dressed off so that it is difficult to locate the joint. The difficulties of die-casting aluminum appear to have been overcome, and there are several companies that claim to successfully die-cast this metal. Another quite recent development is the subjecting of sand castings to very high pressures in order to render the metal more dense and to increase its strength; the machining qualities are also improved. High alloy rods are now rolled in practically all commercial sizes. In the past commercial aluminum rod has been largely a drawn product. By the rolling process a more homogeneous material is produced than is attainable by the rolling process, making available a good machining aluminum rod in all commercial sizes for automatic machine and turret lathe products.

Aluminum electric transmission cable, steel-reinforced, has been in commercial use on an extensive scale for the past few years. Steel reinforcement was adopted in order to reduce the greater sag of the line incident to the greater coefficient of expansion and inferior tensile strength as compared with copper cable. It has been found feasible to construct these cables with any standard number of strands and to meet required conditions of strength and sag. To-day many of the most modern transmission lines are built with this cable.

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